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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XII. ANTIFREEZE PROPERTIES OF TERNARY AQUEOUS SOLUTIONS CONTAINING *LEVO*-2,3-BUTANEDIOL AS A MAJOR COMPONENT[1]

BY K. A. CLENDENNING[2] AND D. E. WRIGHT[3]

Abstract

Freezing point, viscosity, and boiling point data are presented for aqueous solutions of *levo*-2,3-butanediol containing methanol, ethanol, ethylene glycol, and tetrahydrofurfuryl alcohol as third components. All four ternary systems show freezing points of −50° C. and lower over a considerable range of compositions. Among the compounds tested as third components, methanol was most effective as a thinning agent and accessory freezing point depressant. The data indicate that 20% methanol–40% butanediol–40% water is suitable for use at temperatures as low as −50° C.

Introduction

Judging from the variety of antifreeze commodities sold on the civilian market from year to year, the price of antifreeze contributes quite as much to its popularity as its physical properties. It is generally agreed that the properties of ethylene glycol render it particularly suitable for use as an antifreeze. On a basis of initial cost, this chemical has remained the most expensive of all established antifreeze compounds by a considerable margin. For this reason more than any other, it has not proved universally acceptable to motorists.

The war-time removal of ethylene glycol and glycerol from the home market led to a more general use of non-permanent antifreeze compounds by civilians. During this period, the production and properties of *levo*-2,3-butanediol have been studied intensively. Present indications are that this compound may be usefully employed as a non-volatile antifreeze (1, 8). When surplus agricultural products are employed as the fermentation substrate, it is considered possible to market this compound at a lower price than that of ethylene glycol either at the present time or at any period since it came on the market two decades ago (1).

It has already been shown that protection against freezing is provided down to −40° C. by 60 to 70% *levo*-2,3-butanediol solutions (1). In view of

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the high viscosity of concentrated butanediol solutions at low temperatures, the 50% solution was selected as most suitable for use in automobile radiators. This strength has been used in automobiles throughout the winters of 1944-45 at Ottawa and of 1945-46 at Ottawa and Saskatoon. By correcting evaporation losses with water throughout the winter, adequate protection was provided, as with other permanent-type compounds. A practical device, based on the relation of flow-time to concentration and temperature, has been provided for the testing of butanediol solutions after use in radiators (9).

Reference has already been made in the technical literature to the usefulness of ternary antifreeze solutions and a number of patents have been granted for radiator fluids of this type (10). Freezing point data have been provided for the systems methanol–glycerol–water and methanol–ethylene-glycol–water by Feldman and Dahlstrom (6) and Conrad, Hill, and Ballman (3), respectively. Viscosity data for ethanol–glycerol–water solutions at 25° C. have also been presented by Ernst, Watkins, and Ruwe (5). The advantages claimed include lowering of the cost and viscosity by the alcohol, and lowering of volatilization losses by the non-volatile component; thus the advantages of each agent are retained to some extent while the objectionable characteristics are minimized.

It must be borne in mind, however, that the third component alters the physical properties that provide the basis for practical tests of freezing point protection in binary aqueous solutions. If the third component is volatile, it is also necessary to add this component as well as water in correcting volume losses.

The purpose of the present investigation was the provision of radiator solutions suitable for use in extremely cold weather (−45° to −50° C.) by blending aqueous *levo*-2,3-butanediol* solutions with other antifreeze chemicals. Methanol, ethanol, ethylene glycol, and tetrahydrofurfuryl alcohol were selected for study as third components, and the suitability of the various combinations was assessed by measurements of freezing point, viscosity, and boiling point.

Materials and Methods

Tetrahydrofurfuryl alcohol (Eastman Kodak) was purified by distillation through a Stedman column, and the fraction having a refractive index of 1.4505 at 25° C. was retained for use. Preparation of the remaining chemicals and methods employed in determining freezing point, viscosity, and boiling point have already been described (1).

Data for the ternary diagrams were derived from sets of curves for two- and three-component series. The viscosity data plotted on triangular coordinates are based on a smaller number of determinations than the freezing point figures and should therefore be regarded as approximations. They are considered sufficiently accurate to establish the general tendencies under discussion.

* *Hereafter, the term "butanediol" will be understood to refer to levo-2,3-butanediol.*

Results and Discussion

Methanol–Butanediol–Water

Freezing Point

The outstanding features of the freezing point diagram for this system arise from the effectiveness of methanol as an accessory antifreeze, the range of compositions capable of withstanding −50° C. being much wider than in any other system studied (Fig. 1). The ternary solution containing 50% water and 15% methanol provides ample protection against freezing to temperatures of −40° C. With water contents of 20 to 40% and a methanol content of 10%, the freezing point is below −45° C. 5% Methanol–60% butanediol–35% water freezes at approximately −50° C. The curvature of the upper tie-lines indicates lower freezing points for ternary systems of high water content than would be expected from strictly additive effects of the two freezing point depressants. There is earlier evidence of this latter property in the freezing point data of methanol–glycerol–water (6) and some indications of it in the system methanol–ethylene-glycol–water, at least for compositions freezing at −40° to −50° C. (3).

Viscosity

Interpretation of Fig. 2 is considerably facilitated by assuming that methanol and butanediol undergo hydration (1, 7). Within series of compositions containing 40% or more of water, and in which butanediol is present in constant amount, replacement of part of the water with methanol does not reduce the viscosity appreciably. The viscosities of 40% butanediol–60% water, and 20% methanol–40% butanediol–40% water, for instance, are practically identical.

The complications introduced by hydration are well illustrated by the pronounced curvature of the 2.5-centistoke tie-line, which includes compositions containing 20% butanediol at widely different water contents. Beginning with 20% butanediol–80% water, substitution of methanol for water at first increases the viscosity. As the proportion of methanol is further increased, the viscosity decreases. The present data signify that considerable reduction in viscosity is effected by substitution of methanol for part of the butanediol at uniform water contents, e.g., 40%. This change results from the difference in viscosity of hydrated methanol and butanediol, which difference is less pronounced than that shown by the anhydrous chemicals.

At 20° C. the viscosities in centistoke units for 40% butanediol–60% water, 60% ethylene glycol–40% water, and 20% methanol–40% butanediol–40% water are 5.24, 4.71, and 5.17, respectively, or approximately one-half that of 60% butanediol–40% water at the same temperature (10.8 centistokes). It has already been shown that 50% butanediol is the most suitable concentration for use as a binary aqueous antifreeze, higher concentrations being undesirably viscous, and lower concentrations having freezing points above −30° C. (1). On mixing 50% aqueous butanediol solution with methanol in the ratio of 4 : 1 by weight to obtain the ternary solution 20% methanol–40%

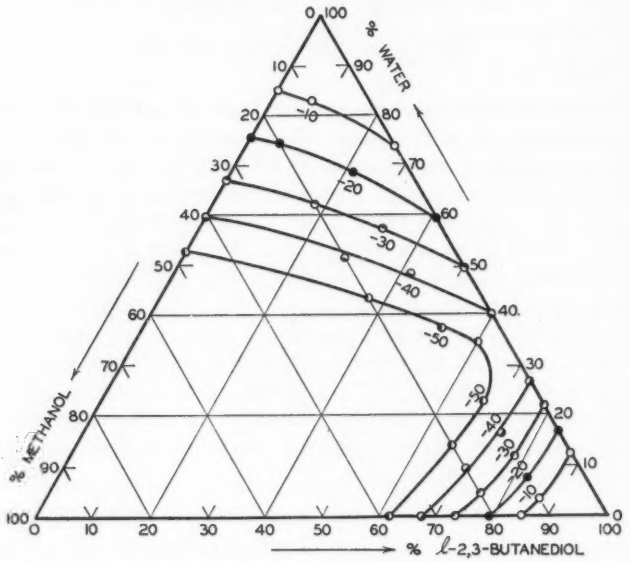

FIG. 1. *Freezing points of aqueous l-2,3-butanediol–methanol solutions.*

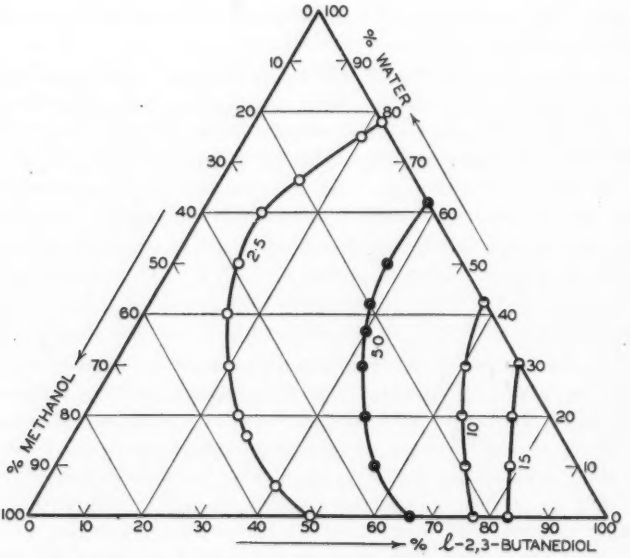

FIG. 2. *Kinematic viscosity of aqueous l-2,3-butanediol–methanol solutions at 20° C., expressed in centistokes.*

butanediol–40% water, the freezing point is reduced to −50° C. and the viscosity at 20° C. is reduced to less than half that of 60% butanediol–40% water and almost to that of 60% ethylene glycol–40% water.

Boiling Point

The boiling point of methanol–butanediol–water solutions is strongly influenced by methanol content (Fig. 3). Over the range 30 to 50%, water

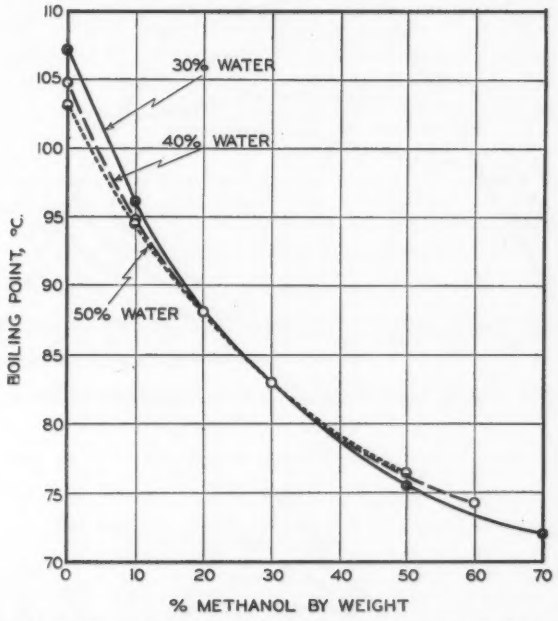

FIG. 3. *Boiling points of aqueous l-2,3-butanediol–methanol solutions.*

content has little effect on the boiling point of systems having identical methanol contents. The boiling points of the ternary systems are slightly higher than those of binary aqueous solutions of the same methanol content: e.g. 20% methanol–40% butanediol–40% water, 88.2° C.; 20% methanol–80% water, 86.2° C. The boiling points of the ternary systems containing methanol (Table I) are substantially higher than that of 50% aqueous methanol solution.

TABLE I

FREEZING POINT AND BOILING POINT DATA FOR BINARY AND TERNARY AQUEOUS METHANOL SOLUTIONS

Composition	F.p., ° C.	B.p., ° C.
10% methanol–50% butanediol–40% water	−48	94.7
10% methanol–90% water	− 6	91.7
20% methanol–40% butanediol–40% water	Below −50	88.2
20% methanol–80% water	−15	86.2
50% methanol–50% water	Below −50	76.5

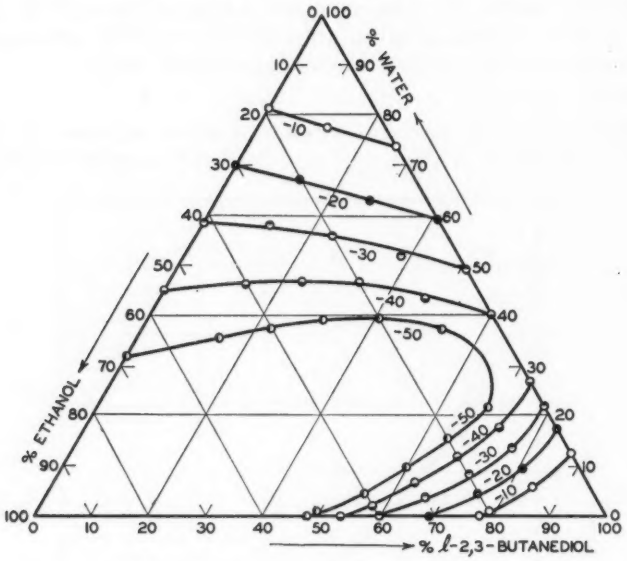

FIG. 4. *Freezing points of aqueous l-2,3-butanediol–ethanol solutions.*

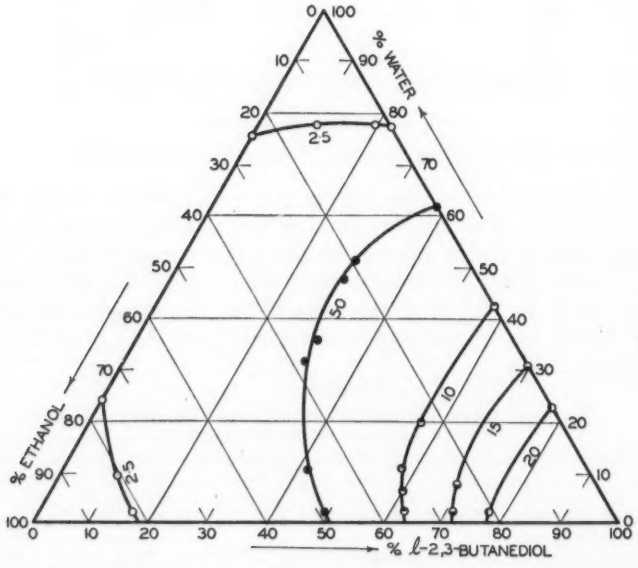

FIG. 5. *Kinematic viscosity of aqueous l-2,3-butanediol–ethanol solutions at 20° C., expressed in centistokes.*

Ethanol–Butanediol–Water

Freezing Point

Fig. 4 shows that ethanol is less effective than methanol as a supplementary freezing-point depressant. With 30% water, protection to −50° C. is provided by the presence of 10% ethanol. A slightly higher freezing point is shown by the system 20% ethanol–40% butanediol–40% water, which has the advantage of higher water content and fluidity. Apparently there are no ternary ethanol systems of the present type that have freezing points below −50° C. when the water content is 40% or higher. Larger amounts of ethanol are required in reducing the freezing point of the anhydrous diol to a standard extent than with methanol, as would be expected from their molecular weights.

Viscosity

Considerable similarity is shown in the viscosity diagrams for the ternary methanol and ethanol systems (Figs. 2, 5), the principal difference being the

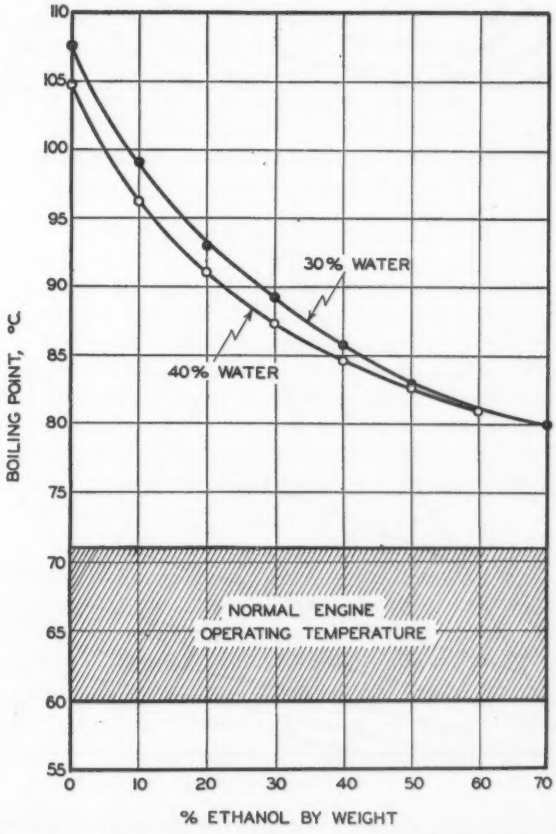

FIG. 6. *Boiling points of aqueous l-2,3-butanediol–ethanol solutions.*

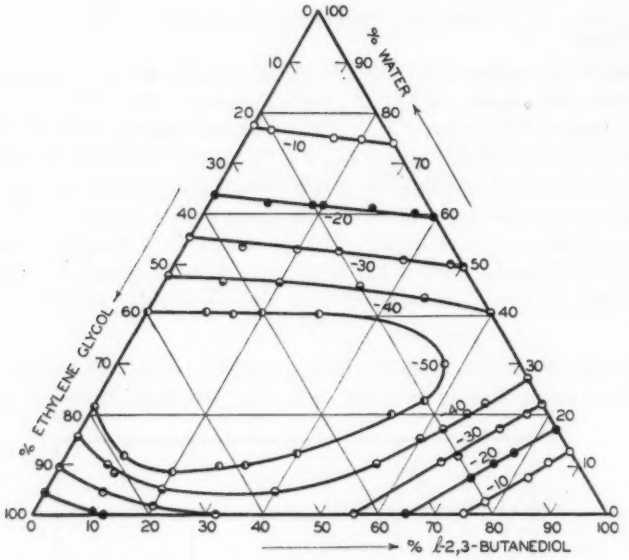

FIG. 7. *Freezing points of aqueous l-2,3-butanediol–ethylene-glycol solutions.*

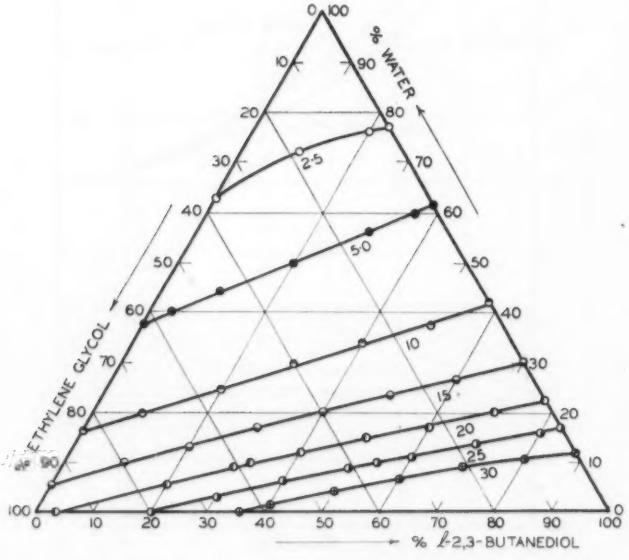

FIG. 8. *Kinematic viscosity of aqueous l-2,3-butanediol–ethylene-glycol solutions at 20° C., expressed in centistokes.*

consistently higher viscosity values shown in ethanol systems at equivalent percentages by weight. General agreement is also shown between the data of Fig. 5 and the viscosity data of Ernst, Watkins, and Ruwe for ethanol–glycerol–water at 25° C. (5). Aqueous solutions of ethanol–butanediol having a viscosity of 5 centistokes at 20° C. and a freezing point of −50° C. were characterized by water contents below 40%, and by approximately equal proportions of ethanol and butanediol.

Boiling Point

Aqueous ethanol solutions of low water content have higher boiling points than methanol solutions of corresponding concentration (4). There is little difference between the two ternary systems in this respect, however, so long as the total alcohol content does not exceed 20% (Figs. 3, 6). The present data provide no evidence of azeotropic mixtures of high boiling point in either of these ternary systems—addition of methanol or ethanol in appreciable amounts reduces the boiling point below 100° C. The ternary ethanol solutions have higher boiling points than are shown by binary aqueous solutions of the same ethanol content. The difference in boiling point of ternary and binary ethanol solutions of the same freezing point are particularly noteworthy: 10% ethanol–50% butanediol–40% water (f.p., −45° C.) boils at 96.3° C. while 65% ethanol, having the same freezing point, boils at 80.5° C.; 20% ethanol–40% butanediol–40% water, which has approximately the same freezing point as the foregoing solutions, boils at 91.2° C.

Ehylene-Glycol–Butanediol–Water

Freezing Point

For systems containing 50% and higher percentages of water, ethylene glycol is less effective than ethanol as an accessory freezing point depressant (Figs. 4, 7). The −40° C. tie-line, however, passes through points representing almost identical compositions in these two diagrams. With water contents of 20 to 40%, reduction of the freezing point to −50° C. requires larger percentages of ethylene glycol than of either methanol or ethanol: at 40% water, 30% ethylene glycol is required; with 30% water, 15% ethylene glycol suffices (Fig. 7). In the absence of water, the minimal freezing point value of the mixed diols is approximately −35° C.

Viscosity

The outstanding feature of the viscosity diagram (Fig. 8) is the regularity with which this property is altered with changing proportions of the two freezing point depressants, regardless of the water content. The data show that the viscosity of aqueous butanediol solutions cannot be reduced to any great extent by small additions of ethylene glycol, e.g., 10 to 20%.

Figs. 9 and 10 show the effect of butanediol and ethylene glycol contents on the low temperature viscosities of systems containing 40 and 30% water, respectively. With 40% water the viscosity at −50° C. rises sharply with decreasing ethylene glycol content, exceeding 1000 centistokes at a butanediol content of 12.5%. At −40° C., the 40% water series shows a viscosity of

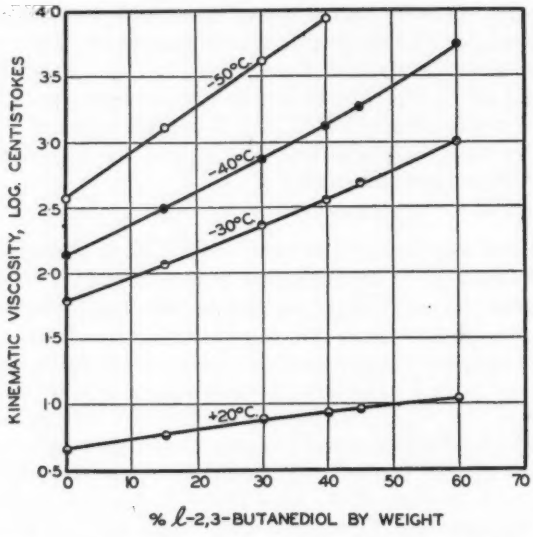

FIG. 9. *Kinematic viscosity at low temperatures of l-2,3-butanediol–ethylene-glycol solutions containing 40% water.*

1000 centistokes at a butanediol content of 35% (Fig. 9), whereas the 30% water series shows a viscosity of 1000 centistokes at a butanediol content of 30% (Fig. 10).

Boiling Point

The boiling point of this system is strongly affected by water content, as in binary solutions of either diol. When the water content is maintained constant at levels of 40% and higher, the boiling point is not changed appreciably by different proportions of the two freezing point depressants, the same applying to the system, tetrahydrofurfuryl-alcohol–butanediol–water.

TETRAHYDROFURFURYL-ALCOHOL–BUTANEDIOL–WATER

Freezing Point

The range of compositions freezing at and below −50° C. is more restricted in this ternary system (Fig. 11) than in those considered previously, for practical purposes being limited to water contents of 30% or less. It is in essentially anhydrous systems that this alcohol shows particular promise as an antifreeze (2).

Viscosity

Aqueous solutions of tetrahydrofurfuryl alcohol are less viscous than aqueous butanediol solutions of corresponding concentration, and the ternary mixtures in general show intermediate values (Fig. 12). The curvatures of the 10- and 15-centistoke tie-lines are attributed to hydration effects operating in the

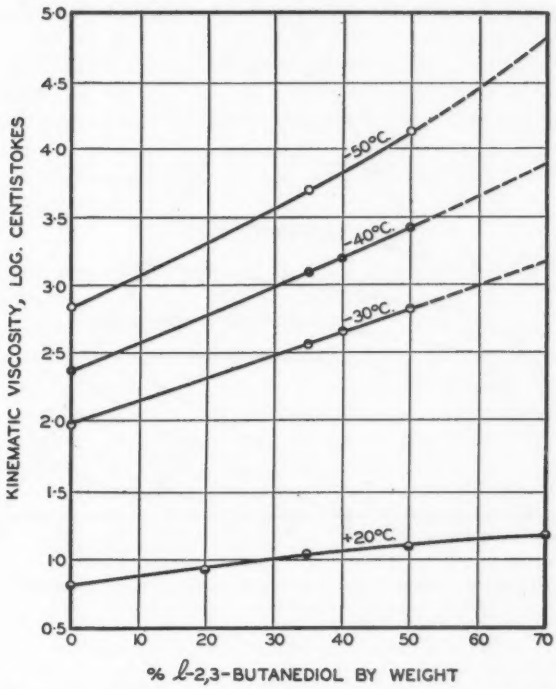

FIG. 10. *Kinematic viscosity at low temperatures of l-2,3-butanediol–ethylene-glycol solutions containing 30% water.*

same manner as in ternary methanol and ethanol systems (Figs. 2, 5). The strong curvature of the 10-centistoke line appears at a relatively low water content. This effect of hydration at low concentrations of water is also apparent in the absence of butanediol: aqueous tetrahydrofurfuryl alcohol solutions show maximal density and viscosity values at water contents of 10 to 20% (2).

Viscosity measurements were made at low temperatures on several aqueous solutions of tetrahydrofurfuryl-alcohol–butanediol freezing at or below −50° C. The values were very similar, however, to those shown by 60% butanediol at the same temperatures.

Conclusions

Among the third components dealt with in this paper, methanol is judged most effective as an accessory freezing point depressant and thinning agent. As little as 5% methanol suffices to reduce the freezing point to −50° C. Greater amounts of methanol are required in reducing the viscosity to that of 60% aqueous ethylene glycol solution, and use of methanol in substantial amounts lowers the boiling point.

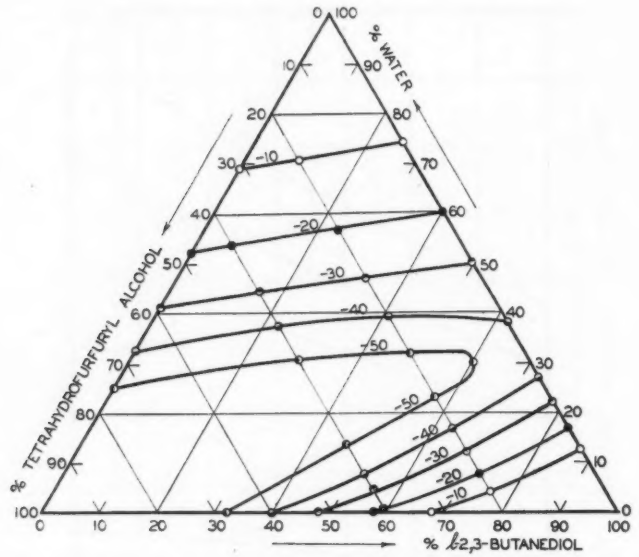

FIG. 11. *Freezing points of aqueous l-2,3-butanediol–tetrahydrofurfuryl-alcohol solutions.*

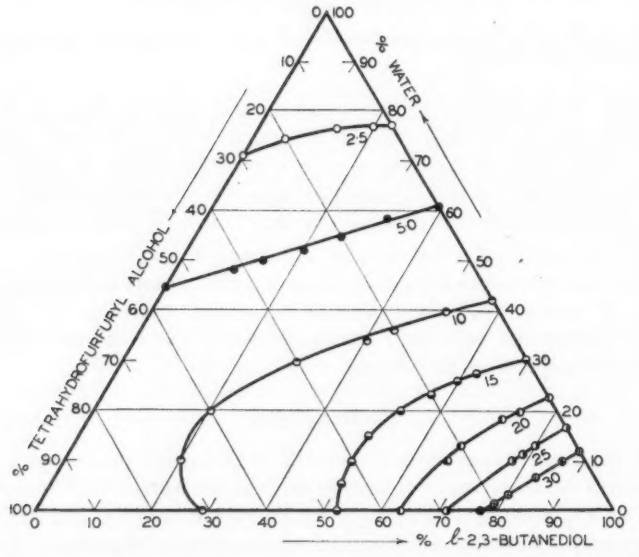

FIG. 12. *Kinematic viscosity of aqueous l-2,3-butanediol–tetrahydrofurfuryl-alcohol solutions at 20° C., expressed in centistokes.*

The ternary solution 20% methanol–40% butanediol–40% water does not freeze at −50° C., has a considerably higher boiling point than aqueous methanol solutions of equivalent freezing point, and is almost as fluid as 60% ethylene glycol at 20° C. On the basis of laboratory tests, this ternary mixture appears suitable for use at temperatures as low as −45° to −50° C. Its practical value as a radiator solution for use under these extreme conditions cannot be fully assessed until it has been exposed to similar conditions in engine cooling systems.

Acknowledgments

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XIII. PURIFICATION OF BY-PRODUCT ETHANOL[1]

By E. L. Tollefson[2], J. A. Wheat[3], and J. D. Leslie[3]

Abstract

Samples of high wines recovered from three whole wheat mashes fermented by *Aerobacillus polymyxa* were fractionated by rectification. It was shown that the high wine from this fermentation resembles that obtained from a yeast fermentation and that a satisfactory industrial ethanol may be prepared by distillation methods. By preparation of derivatives, acetone, diacetyl, and acetic acid were shown to be present in the high wine.

Introduction

Fermentation of carbohydrates by *Aerobacillus polymyxa* produces *levo*-2,3-butanediol as the principal product of commercial value. In addition, a smaller amount of ethanol is produced, which in commercial practice would be of sufficient value to justify recovery. Yields, ratio of diol to ethanol, and other characteristics of the fermentation have been discussed in previous papers of this series (2, 7, 13). The pilot plant process for both fermentation and recovery of products from fermented mash, as developed in these laboratories, has also been described (8, 9).

Ethanol is separated as high wine in the first recovery operation, which consists of stripping fermented mash, at atmospheric pressure, in a conventional type of beer column. The overhead, or distillate, is completely condensed, part being removed as high wine and the remainder returning to the column as reflux. The stripped mash, or slops, is discharged from the bottom of the column.

The overhead product contains 60 to 80% by volume of ethanol, as well as small amounts of several other substances that must be partially or completely removed if the ethanol is to meet specifications for industrial use. These impurities are formed mainly during the fermentation, but it is conceivable that some may result from chemical reactions taking place during the stripping operation.

Batch rectification of high wine in the pilot plant had shown that impurities occurred in the fractions distilled off both before and after the ethanol fraction; in particular a two phase material appeared between the ethanol and water fractions. This indicated that the material contains impurities analogous to those present in the high wine recovered from a yeast fermentation. In this industry high wine is separated by rectification into four fractions: aldehydes,

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ethanol, fusel oil, and water. This separation may be carried out on either a continuous or batch basis and usually yields a pure ethanol–water product of approximately the azeotropic composition. For continuous operation, two (10) or three (4) distillation columns are required, whereas for batch operation a still pot and one column suffice.

The purpose of the present work was (i) to determine the nature and amounts of the impurities in the high wine, and (ii) to investigate the conditions for obtaining a satisfactory industrial ethanol.

Methods and Materials

The general method of investigation was to fractionate high wine by batch distillation under carefully controlled conditions, and to analyse the product fractions for various components as described below. Some of the fractions were again rectified in a smaller apparatus, and individual compounds were identified by boiling points, refractive indices, and preparation of derivatives. Samples of high wine recovered from three fermentations were fractionated. The fermentation conditions differed in that in the first run half of the mash was aerated with 2.6 c.f.m. per 100 gal. for 48 hr., in the second the rate of aeration was the same but was continued for 72 hr., while the third was not aerated. All fermentations showed only a slight trace of contamination and all gave efficiencies of over 90%.

Rectification was carried out in an iron column, 3 in. in diameter by 2 ft. high, packed with 24 stainless steel Stedman plates, and heavily lagged with asbestos. The column was mounted on a jacketed, steam heated, copper, still pot of 16 litres capacity. Into the top of the column was sealed a glass distilling head (shown in Fig. 1) to permit the setting and measurement of any desired reflux ratio. Two 50 cm. Liebig condensers provided ample condensing capacity. All fractionations were carried out at atmospheric pressure and observed boiling points were corrected to 760 mm.

Reflux ratios were measured as follows. The column was first brought to equilibrium under total reflux with stopcock x open and stopcock y closed. Then x was closed and the time, t_1, for the cup to fill to level B was measured with a stopwatch. From this measurement and the known volume of the cup between levels A and B, the total condensate per minute could be computed. After draining the cup through x, y was opened and adjusted to give the desired take-off. Next, to determine the reflux ratio, x was again closed and the time, t_2, for the cup to fill as before was measured. The ratio of reflux to take-off is given by the expression $t_1/(t_2 - t_1)$. A slight error is introduced by the increased flow through y when the level in the cup rises from A to B, but the effect was not important in this work. During operation of the column, stopcock x was left open and the product was drawn off through y.

In Run 1, 8 kgm. was charged to the still pot, heated to boiling and the column operated at total reflux until a constant top temperature indicated that equilibrium had been established. Then the take-off stopcock (y in

Fig. 1) was opened and distillate collected at an initial reflux ratio of 12. While the top temperature was rising, samples large enough for complete analysis were taken, each of which represented the average composition over a range of temperature.

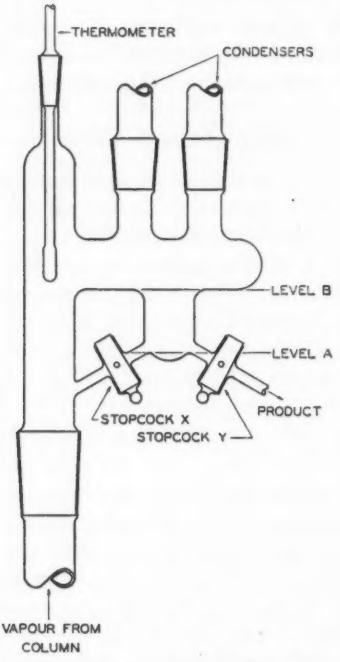

FIG. 1. *Distillation head used in rectification of high wine.*

When the top temperature reached 78.2° C., indicating a composition corresponding to the ethanol–water azeotrope, the reflux ratio was decreased to 5 by increasing the rate of distillate take-off. The rate of boiling in the still pot was kept as constant as possible throughout the entire rectification. After removal of the main ethanol fraction in approximately 500 ml. lots, the temperature again rose, and at this point the reflux ratio was increased to 7. This value was maintained until the temperature reached 100.0° C., showing that the distillate was water. When the amount of material left in the still became so small that the rate of boiling could not be maintained, rectification was stopped, and the column holdup was allowed to drain back to the pot. This material constituted the last sample.

The procedure for Run 2 was the same as that described above except that the charge was 10 kgm. and a reflux ratio of 10 was used at temperatures below 78.2° C., and one of 2 above 78.2° C. In Run 3 a charge of 10 kgm. was distilled at an initial reflux ratio of 25. Then, when the temperature

reached 78.2° C. this was reduced to 1. When the temperature began rising after the removal of the ethanol fraction the reflux ratio was increased to 30.

All samples were analysed for titratable acidity, esters, fusel oil, and aldehydes, and in the third fractionation several samples were analysed for ethanol. These analyses were chosen since they are the basis for industrial ethanol specifications. The analytical procedures were as follows.

Acids.—A 25 gm. sample was titrated with 0.1 *N* sodium hydroxide to a phenolphthalein end-point. Results are reported as milliequivalents per 100 gm. of distillate.

Esters.—Excess 0.1 *N* sodium hydroxide was added to the previously neutralized sample, the mixture was shaken, allowed to stand overnight, and then was back titrated with 0.1 *N* sulphuric acid. The difference between the base added and that neutralized by acid was taken as the amount required to saponify the esters, and the results are expressed as milliequivalents per 100 gm. of distillate.

*Fusel oil.**—This analysis is a colorimetric one for the determination of the fusel oil content of industrial ethanol. Since it is not specific for fusel oil and can be used only for low concentrations it was applied only to samples of the ethanol fraction. The reagent is prepared by mixing 1 gm. of salicylaldehyde with 100 ml. of 85%, fusel-oil–free, ethanol. To 1.0 ml. of sample, 0.1 ml. of reagent and then 2 ml. of concentrated sulphuric acid was added in such a way as to produce layering. The mixture was shaken vigorously and allowed to stand for five minutes. Colours ranging from lemon yellow, through orange, to red indicated 5 to 30 mgm. of fusel oil per 100 ml. of sample. By diluting the original sample, the range of fusel oil content was extended to 150 mgm. per 100 ml.

*Aldehydes.**—Silver ammonium hydroxide reagent was prepared by adding 1 ml. of 8.25% sodium hydroxide to 1 ml. of 8.25% silver nitrate, and then ammonium hydroxide (specific gravity 0.90) until the precipitate just dissolved. One millilitre of the freshly prepared reagent was added to 10 ml. of sample, and, after shaking, the mixture was allowed to stand in the dark for one hour. Formation of a white precipitate upon addition of 1 ml. of 10% sodium chloride solution indicated the presence of unreduced silver, and a trace of cloudiness satisfied the specification.

Ethanol.—The sample to be analysed was first diluted to give a solution containing less than 3.6% ethanol. Twenty-five millilitres of this solution was added to 25 ml. of water and four drops of 40% sodium hydroxide in a 500 ml. round bottom flask. About 35 ml. was distilled at constant volume, and collected in a 50 ml. volumetric flask. The distillate was made up to 50 ml. and 2.0 ml. of this added to 15 ml. of 0.2 *N* potassium dichromate and 25 ml. of 50% sulphuric acid in a pressure bottle. The pressure bottle was capped and placed in a bath of boiling water for 20 min. After cooling, 3.5 ml. of 30% potassium iodide was added and the liberated iodine titrated

* *Unpublished methods from Joseph E. Seagram and Sons, Inc.*

with 0.2 *N* sodium thiosulphate using starch as an indicator. The concentration of ethanol in the original sample was calculated from the difference between blank and sample titrations. Since aldehydes interfere in this determination they were removed prior to the distillation step by precipitation with 2,4-dinitrophenylhydrazine.

Experimental Results

Rectification of High Wines

The important characteristics of the three high wines that were fractionated are shown in Table I. The densities at 20° C. were calculated from specific gravities determined with a Westphal balance. The difference in acid and ester contents are believed to be attributable to the conditions of fermentation. Since it is known (1) that aeration of fermenting mashes increases the production of organic acids and decreases ethanol formation the results in Table I are not unexpected.

TABLE I

CHARACTERISTICS OF THE HIGH WINES USED FOR FRACTIONATION

Run No.	Ethanol, % by weight	Density, gm./ml., 20° C.	Acid, m.e./100 gm.	Ester, m.e./100 gm.
1	66.9	0.8672	0.23	1.92
2	65.7	0.8677	0.79	2.95
3	66.6	0.8697	0.17	1.01

The change in boiling point throughout the distillations and the results of the analyses for acids and esters of the various fractions are shown in Figs. 2, 3, and 4. In Fig. 4 the ethanol concentration is also shown. In the range 4 to 68% distilled this was estimated from specific gravities determined with a Westphal balance and the other values are the results of chemical analyses of samples treated with 2,4-dinitrophenylhydrazine.

In Table II the mean acid, ester, and fusel oil contents are shown for the samples that had a satisfactory aldehyde content. A comparison of these results with the corresponding values for the original high wines (Table I) shows that strict proportionality does not hold. The discrepancies are attributed to differences in the reflux ratios and to possible variations in the chemical composition of the high wines. An additional fact, not shown in Table II, is that the ethanol fractions in Runs 1 and 2 had a trace of yellow colour; whereas this was not observed in Run 3. The yellow colour is known to be due to the presence of diacetyl, and is discussed further in the next section.

Identification of Components in High Wine Fractions

The boiling point curve for Run 2 indicated a considerable amount of some material boiling at 55 to 58° C. In order to identify this compound the fractions collected in the temperature range 52.8 to 58° C. were mixed and

TABLE II

CHARACTERISTICS OF THE ETHANOL FRACTION THAT MET ALDEHYDE SPECIFICATIONS

Run No.	Acid, m.e./100 gm.	Ester, m.e./100 gm.	Fusel oil, mgm./100 ml.	Distillation range, %
1	0.05	1.0	24	11.0–70.5
2	0.40	1.6	35	14.5–69.5
3	0.04	0.1	15	6.9–67.5

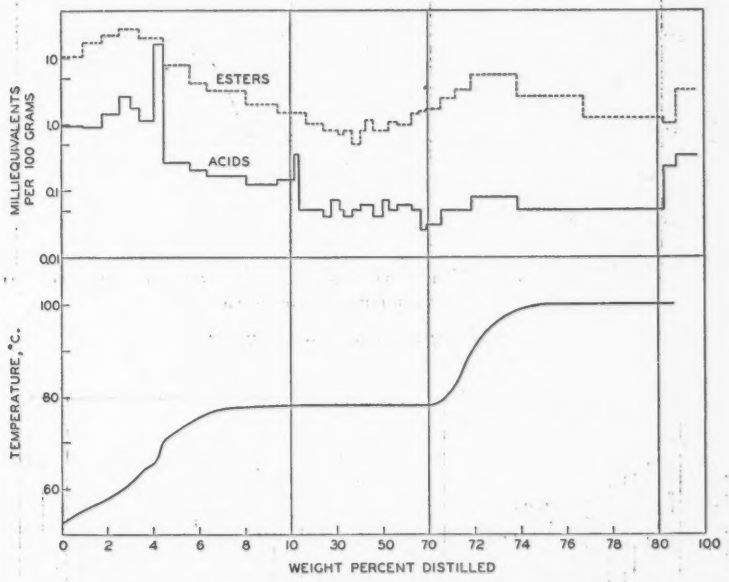

FIG. 2. *Distillation curves of Run 1.*

refractionated in a small Stedman column. A boiling point of approximately 55° C., maintained throughout the main part of the distillation, was a good indication that acetone was present. Refractive indices of the different fractions indicated that about 65% of the material redistilled was acetone. This corresponded to about 2% of the high wine. To prove that the product was acetone the 2,4-dinitrophenylhydrazine derivative was prepared. It gave a melting point of 126° C., which is the value given in the literature (12) for acetone 2,4-dinitrophenylhydrazone. A mixed melting point with an authentic derivative showed no deviation from this temperature, thus proving that the compound was acetone.

Since the odour of the residual liquid from the above redistillation suggested the presence of acetic acid the *p*-bromophenacyl ester was prepared from the neutralized residue and *p*-bromophenacyl bromide. After purification by

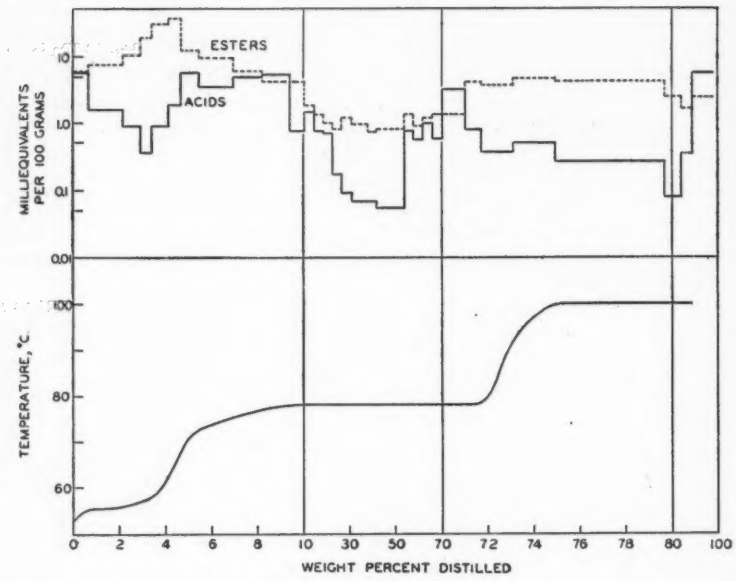

FIG. 3. *Distillation curves of Run 2.*

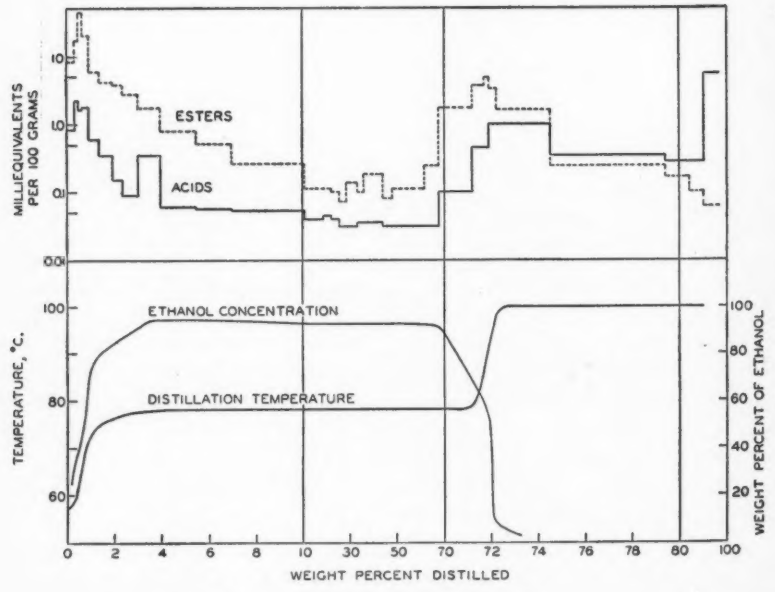

FIG. 4. *Distillation curves of Run 3.*

recrystallization, comparison of this derivative with an authentic derivative proved that acetic acid was present.

The fraction of high wine collected from 58° to 68° C. had the characteristic odour of esters. For this reason a saponification was carried out by adding sodium hydroxide solution and allowing the mixture to stand overnight. This was followed by a determination of the volatile fatty acids by the method of Hillig and Knudsen (5). When the required distillation had been completed the formic acid present was determined by Lozzari's method (10), although formic acid had not been identified. The result showed the presence of only a small amount. The volatile acid analysis proved that acetic was the main acid constituent.

Throughout the complete series of fractions collected in Runs 1 and 2 a yellow colour was observed. This was thought to be due to diacetyl and accordingly a phenylhydrazine derivative was prepared. The purified, crystalline product had the same melting point as an authentic sample of diacetyl bisphenyhydrazone. A mixed melting point, showing no deviation from this temperature, proved the presence of diacetyl. It was then possible to devise a method for purifying the ethanol. Enough sodium hydroxide was added, in pellet form, to neutralize the acids, saponify the esters, and polymerize the diacetyl. When these reactions were complete a simple distillation gave a colourless product of negligible acid and ester content. The values given in Table II were obtained before treatment with sodium hydroxide.

Following the removal of the ethanol fraction in the main rectification there was a sharp rise in the top temperature. This was accompanied by the separation of an oily emulsion, which, in Runs 1 and 2, continued to come over until the temperature reached 100° C. A portion of this emulsion was extracted with ether over anhydrous sodium sulphate, and the ether layer separated and distilled. Two, small, constant temperature fractions were obtained, one boiling at 92° C. and the other at 127° C. The first fraction, which separated into two layers, appeared to be the *n*-butanol–water azeotrope (boiling point 92.25° C. (6)) or the isoamyl-alcohol–water azeotrope (boiling point, 95.15° C. (6)). A 3,5-dinitrobenzoate derivative was prepared from the upper layer, and repeated crystallization gave a constant melting point of 52.5° C. The 3,5-dinitrobenzoate of *n*-butanol melts at 64° C. (12) and that of isoamyl alcohol at 62° C. (12). Therefore the product obtained was neither of these. Further identification work on this unknown could not be continued because of the small amount available.

The fraction boiling at 127° C. had a refractive index of 1.4079 at 25° C. The boiling point and refractive index indicated that the material might be either 2-methylbutanol-1 or 2-methylpentanol-3. It was found to form a 3,5-dinitrobenzoate, which, on repeated recrystallization, had a constant melting point of 82° C. The melting point of the 3,5-dinitrobenzoate of 2-methylbutanol-1 is 62° C. (12) and that of 2-methylpentanol-3 is 85° C. (3). A sample of the latter was not available so it was not possible to do a mixed melting point.

The boiling point curve for Run 3 gave no indication of the presence of acetone. In order to prove its presence in this high wine more of the low boiling fractions were required. Four kilograms of the original high wine was distilled in five 800 gm. batches in a glass column packed with $\frac{1}{8}$ in. glass helices. Each batch was distilled with a reflux ratio of approximately 2 and the distillation was continued until 125 ml. had been collected. The 557 gm. of combined distillate was refractionated in a glass column 13 mm. in diameter, packed with 60 cm. of $\frac{1}{8}$ in. glass helices. The method of operation of both these columns was similar to that described above, in that the vapours were totally condensed, a portion of the condensate removed, and the rest returned to the column as reflux. The reflux ratio could not be measured but the rate of product removal could be carefully controlled. This last feature is an advantage over a cold finger condenser where the rate of take-off is controlled by adjusting the heat input to the still and water rate through the condenser. Under total reflux an initial temperature of 49° C. was obtained, while that obtained in the Stedman column was 57° C. The distillation curve is shown in Fig. 5. A constant temperature of 56.3° C. was observed in the range 0.8 to 3.0% distilled; this material was 0.31% of the high wine. The 2,4-dinitrophenylhydrazine derivative of this fraction was prepared and found to have a melting point of 126° C., which did not change when the product was mixed with an authentic sample of acetone 2,4-dinitrophenylhydrazone.

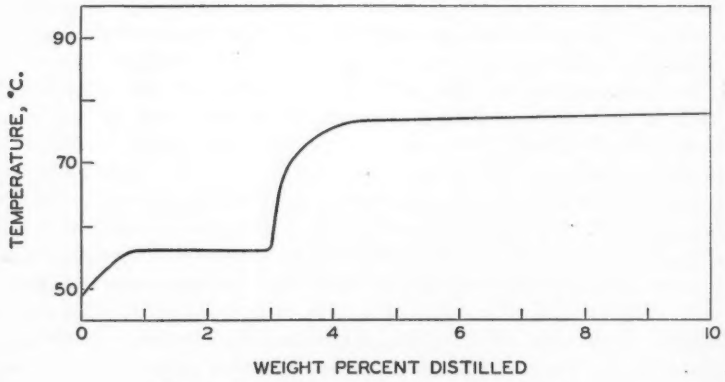

FIG. 5. *Distillation curve of aldehyde fraction.*

One sample of Run 3 boiling at 92° to 98.2° C. separated into two layers on condensation. The fusel oil layer was 0.015% of the high wine. This quantity was insufficient for further identification other than by solubility tests, which showed that it consisted of alcohols, aldehydes, and ketones with fewer than nine carbon atoms (12).

The presence of diacetyl in Run 3 was indicated by a characteristic yellow colour but was not proved by preparation of derivatives. In this run, how-

ever, only fractions boiling below 78.2° C. were coloured; this indicated that the diacetyl had been removed in the early part of the rectification. This difference is believed due to the higher reflux ratios used and to a lower initial content.

Discussion

The results presented above show that the high wine from a whole wheat mash fermented by *A. polymyxa* can be fractionated by distillation to give a low boiling fraction high in aldehydes, ketones, acids, and esters, a high boiling fusel oil fraction, and in between a fraction consisting of relatively pure ethanol at approximately the azeotropic composition. Thus, except for the presence of diacetyl this high wine has the same general composition as that obtained from a yeast fermentation, and can be purified by similar methods.

The average values of acid and ester in high grade industrial ethanol are 0.02 to 0.08 and 0.12 to 0.38 m.e. per 100 gm. of 95% ethanol.* From Table II it is seen that the acid content of Run 2 and ester content of Runs 1 and 2 are above these values. Although no information on the fusel oil content of industrial ethanol was available it is believed that the product of Run 2 is also high in fusel oil. The aldehyde contents of all materials listed in Table II were satisfactory; hence the product of Run 3 was satisfactory in all respects. It is of interest to know the percentages of total ethanol contained in these fractions. From the data of Tables I and II, and, taking the ethanol content of the rectified ethanol as 93%, a simple calculation shows that the percentages of total ethanol recovered were: 82.7% in Run 1, 77.9% in Run 2, and 84.5% in Run 3. Most of the remaining ethanol could, of course, have been recovered by further rectification of the other fractions.

The ethanol products of Runs 1 and 2 were also unsatisfactory because of a yellow colour, caused by diacetyl. It is thus apparent that further purification of these two products was necessary. It was proved that diacetyl can be removed by distillation over sodium hydroxide. The results of Run 3 indicate also that it can be removed by more efficient rectification. Although diacetyl boils at 88° C. it is removable in the aldehyde fraction because of its solubility properties. Either the addition of sodium hydroxide or more complete rectification would also reduce the acid and ester contents of the ethanol fractions. The choice of method to be used would depend on economic considerations. If the high wine were purified batchwise, sodium hydroxide could be added to the high wine charge, or to the first ethanol product. The latter procedure would require a redistillation, but would decrease the hydroxide consumption since less acid and ester would be present. In a continuous process, hydroxide could be added to the high wine feed or to the column from which the final product is removed.

* *By courtesy of Joseph E. Seagram and Sons, Inc.*

Acknowledgments

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XIV. BUTANEDIOL ANALYSES FOR PROCESS CONTROL[1]

By J. D. Leslie[2] and A. Castagne[3]

Abstract

The chemical determination of 2,3-butanediol in fermented whole wheat mashes and in certain materials from the recovery process has been investigated from the point of view of process control. The method of analysis involved extraction with *n*-butanol followed by estimation of the butanediol with periodate oxidation. Errors in both parts of the method were estimated and correction factors determined for the various types of materials. The factors recommended are: 1.039 for pure diol solutions and 1.067 for all other materials. Formulae are given for converting analytical results on beer to a basis of whole mash or beer-still slops. These calculations require a knowledge of the insoluble solids contents of the mash or the slops concerned.

Introduction

The method of analysis for 2,3-butanediol discussed in this paper has been found, in general, to be the most suitable in routine work. It consists of two steps: extraction of diol with *n*-butanol and determination of diol in the extract by periodate oxidation. The details of this method were developed by the Department of Biochemistry, University of Wisconsin.* It was applied there mainly to analysis of laboratory cultures, and an extraction coefficient of 96% was reported. During the early work in these laboratories the extraction coefficient was given little attention, since nearly all fermentations were on whole wheat mashes of equal concentration and the results were chiefly of comparative value. It was only after study of the recovery phases of the pilot plant process had begun that analysis of materials other than fermented mash were required. Such materials included crude diol and pure diol concentrates, evaporator syrups, and distillates.

The process referred to for producing 2,3-butanediol was developed at the National Research Laboratories and has been described in various reports and papers (2, 3). So far the work has been confined to whole wheat mashes fermented by *Aerobacillus polymyxa*.

The main purposes of the present work were to examine critically the analytical procedures for diol determination, to supply correction factors for the principal materials in the process, and to give the necessary calculation for applying the analytical results to process control.

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* *Unpublished method.*

Methods and Materials

Butanediol Analysis

Five millilitres of sample and 10 ml. of *n*-butanol, reagent quality, are pipetted into a 15 by 150 mm. test-tube; 6 gm. of anhydrous potassium carbonate is added and the mixture is shaken immediately for at least 15 sec. After standing for 2 to 3 min. (to permit complete hydration of the carbonate), the mixture is shaken for a further 30 sec. to ensure complete extraction of the diol. The carbonate should be almost completely dissolved. The tube and contents are centrifuged long enough to give two clearly separated layers, and then 5 ml. of the butanol layer is carefully pipetted into a 100 ml. volumetric flask, dissolved in distilled water and made up to volume. To a 5 ml. aliquot of diluted extract, in a 25 by 200 mm. test-tube, is added 1.0 ml. of 1.0 *N* sulphuric acid and 5 ml. of 0.01 *M* potassium periodate. After mixing, the tube is loosely capped with a glass stopper and heated in boiling water for exactly 10 min. After cooling, 5 ml. of 0.5 *M* disodium hydrogen phospate is added, the mixture is shaken and 1 ml. of potassium iodide solution (30 gm. per 100 ml.) is added. The liberated iodine is titrated immediately with 0.005 *N* sodium thiosulphate. To correct for oxidizable substances in the butanol a blank determination on 5 ml. of distilled water is made in exactly the same way. The difference between the volumes of thiosulphate required to titrate the blank and the sample is used in calculating the diol content. One millilitre of 0.005 *N* thiosulphate is equivalent to 0.225 mgm. of 2,3-butanediol, and since the original 5 ml. sample is diluted 40 times in the procedure, the diol, in grams per 100 ml. of sample, is given by: ml. of thiosulphate $\times$ 40 $\times$ 20 $\times \frac{0.225}{1000}$ = ml. of thiosulphate $\times$ 0.180. This calculation assumes 100% extraction, and the answer must be multiplied by an empirical correction factor as described in the next section.

Acetoin interferes quantitatively, 88 mgm. of acetoin appearing as 90 mgm. of diol. Ethanol up to 5% and glucose up to 20% do not interfere.

Materials and General Procedure

The materials in which diol estimations are required fall into four classes: (*a*) fermented mashes, beer-still slops, filtrates and beers, (*b*) crude diols from rectification and condensates from high pressure stripping, (*c*) evaporator syrups, (*d*) 'pure' diol concentrates. Some of these materials can be analysed directly as they come from the process, the rest require preliminary treatments as follows.

Mashes and beer-still slops are filtered through No. 1 Whatman paper; filtrates and beers are handled similarly if suspended materials are present. The prepared samples from these materials are essentially the liquid phase of fermented mash and are all called 'beer'. No dilution is made prior to analysis.

Evaporator syrups contain 10 to 20% diol and 30 to 60% solids. Five-gram samples are weighed out, dissolved in warm water, and made up to

100 ml. each. Occasionally a slight residue of fine particles is noticeable, but thorough shaking ensures that a true aliquot of the 100 ml. is taken for analysis.

Crude diol has a concentration of 50 to 70% and requires 20 to 40 times dilution; stripped condensates require two to five times dilution. 'Pure' diol concentrates are treated similarly, the dilution factor varying with the concentration.

These procedures require adjustment of the diol concentration below 3.5% and the soluble solids below 3.0% in the 'prepared' samples.

In determining correction factors for each of the above types of material, the general method was as follows. Known amounts of pure diol were added to a series of known quantities of each type and the series of samples were prepared for analysis as described above. All samples were made up to 100 ml. in volumetric flasks. Materials listed under (*a*) and (*b*) required more dilution during sample preparation than is indicated above, to allow for the added diol. Fifty grams of beer and 1.5 to 2.0 gm. of crude diol were taken per each 100 ml. sample. It is worth noting that all materials were weighed, whereas in routine analysis all but evaporator syrups are measured by volume. The latter procedure is faster and is accurate enough for practical purposes.

Pure diol prepared in the laboratory was used in making up the samples and served also as control. After repeated vacuum rectification over calcium oxide it had the following properties: $n_D^{25} = 1.4305$, b.p. = 178.5° C. at 760 mm. pressure, and $(\alpha)_D^{25} = -12.75°$. Subsequent tests showed this diol to contain 0.45% moisture and 0.94% acetate radical. On the assumption that the acetate was completely hydrolysed when the samples were made up, the purity of the diol was taken as 98.88%.

Each series of prepared samples was analysed by making triplicate extractions followed by single diol determinations on each extract. 'Diol recovered' was plotted against 'diol added' and for each series a linear regression line was fitted to the points by statistical methods. The regression coefficient of each line gave a measure of the required correction factor, and the intercept on the 'diol added' axis gave the diol present in the original material, subject to any systematic error in the analysis.

To make the analytical results applicable to process control, it is necessary to determine total and soluble solids in filtrates and mashes. Weighed samples were air-dried at 100° C. for 48 hr., after which the residual diol in the dried samples was extracted with warm water and determined in the usual manner.

Experimental

Factors Affecting Diol Determination

Because of inconsistent results from the routine plant analyses some parts of the analytical procedure were investigated for errors before the main work was undertaken.

(1) The amount of anhydrous potassium carbonate added to a 5 ml. sample in conjunction with extraction by *n*-butanol was varied from 5.5 to 7.0 gm.

No significant effect was observed but 6.0 gm. is recommended since this is only slightly in excess of the amount required to saturate the sample. To avoid lumping it has been found advisable to shake the samples immediately upon addition of the carbonate.

(2) In blank determinations of diol the time of heating at 100° C. after addition of potassium periodate was varied from 5 to 20 min. The results for two experiments, shown in Table I, indicate a decreasing titre with increasing time of heating. The difference between corresponding values in the two experiments resulted from slight variations in the strengths of the reagents. A suggested explanation for the titre drop is that periodate undergoes slow decomposition during heating. It is therefore essential that the time of heating for blanks and unknowns be kept the same.

TABLE I

EFFECT OF HEATING TIME ON BLANK TITRATION IN 2,3-BUTANEDIOL ANALYSIS

Experiment 1		Experiment 2	
Time, min.	$Na_2S_2O_3$ titre, ml.	Time, min.	$Na_2S_2O_3$ titre, ml.
7	19.10	5	19.56
15	18.86	10	19.45
20	18.68	15	19.30
		20	19.06

(3) After removal from boiling water, samples were allowed to stand for various periods in cold water before addition of buffer. No significant effect was observed.

(4) The time elapsing between addition of buffer and addition of potassium iodide was varied from 10 min. to two hours. Again no significant effect could be detected.

To obtain an estimate of the experimental error in the periodate estimation of diol, duplicate analyses were made on each of two sets of butanol extracts. The means and differences between the duplicates of these results are given in Table II. It is clear that the error in question is negligible.

Effect of Concentration on Direct Determination of Diol

To check the accuracy of the periodate estimation over the usual concentration range, aqueous solutions were prepared containing 0.5 to 3.6% diol. Extraction with *n*-butanol was omitted and, after equivalent dilution, duplicate determinations were made on each sample. To check the results obtained, the experiment was repeated with a new sample of diol of 99.17% purity. Table III gives the data of these tests; the differences between duplicate determinations are recorded as well as the mean recoveries. The results show that high recoveries are obtained with periodate oxidation in dilute solutions. This effect has been noted by previous workers (1) and is not

TABLE II

EXPERIMENTAL ERROR IN DIRECT DETERMINATION OF 2,3-BUTANEDIOL IN BUTANOL EXTRACTS

Pure diol series		Beer series	
Mean diol recovered, gm./100 ml.	Difference between duplicates, gm./100 ml.	Mean diol recovered, gm./100 ml.	Difference between duplicates, gm./100 ml.
1.003	0.000	1.092	0.005
1.233	0.000	1.341	0.000
1.450	0.002	1.503	0.000
1.917	0.000	2.013	0.005
2.313	0.000	2.473	0.004
2.813	0.009	2.889	0.000
Mean diff. = 0.0018		Mean diff. = 0.0023	

TABLE III

EFFECT OF CONCENTRATION ON DIRECT DETERMINATION OF 2,3-BUTANEDIOL

Diol of 98.88% purity			Diol of 99.17% purity		
Conc., gm./100 ml.	Mean recovery, %	Difference between duplicates, %	Conc., gm./100 ml.	Mean recovery, %	Difference between duplicates, %
0.5204	101.1	1.3	0.4972	101.1	2.5
1.0408	99.9	0.6	0.9942	101.6	1.6
1.5612	99.6	0.2	1.4916	100.0	0.3
2.0816	98.8	0.5	1.9888	99.5	0.7
2.6020	98.0	0.0	2.4860	99.1	0.2
3.1224	97.8	0.1	2.9832	98.7	0.3
3.6428	97.5	0.0	3.4804	98.7	0.0

Note.—At 0.5 gm./ml. concentration, difference of 0.03 in titre = difference of 1.3% in recovery.

easily explained. The present work suggests that in dilute solutions there is slight decomposition of the residual periodate and this appears as additional diol in the final answer.

Determination of Correction Factors

To estimate the correction factors for the various types of material the following experiments were carried out as described above: one with pure diol solutions, three with beers, three with syrups, and two with crude diol products. Fig. 1 shows one series of each type of material. The 'diol recovered' was calculated from the means of the several extractions. The final results are summarized in Table IV.

Analysis of variance showed that, among the regression coefficients, only the value for pure diol was significantly different from the others. Hence, one value, 0.9264, is recommended for all materials other than pure diol solutions;

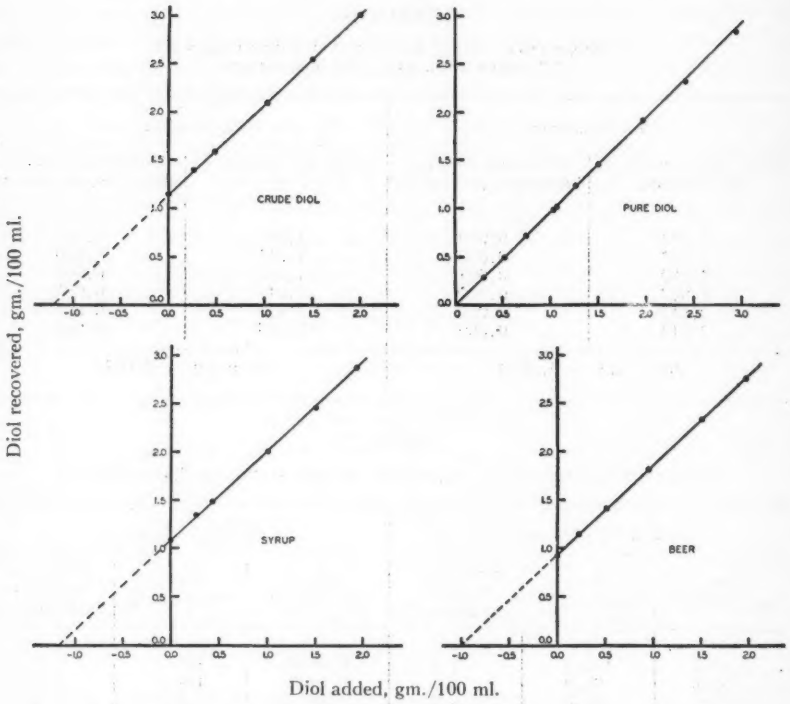

FIG. 1. *Recovery of 2,3-butanediol in analysis of various process materials.*

TABLE IV

CORRECTION FACTORS FOR 2,3-BUTANEDIOL ANALYSIS IN VARIOUS PROCESS MATERIALS

Series	b	S_b	S_e
Beer 1	0.9246	0.0039	
Beer 2	0.9252	0.0067	0.0101
Beer 3	0.9244	0.0068	
Syrup 1	0.9198	0.0085	
Syrup 2	0.9385	0.0066	0.0236
Syrup 3	0.9094	0.0222	
Crude diol 1	0.9303	0.0041	0.0149
Crude diol 2	0.9401	0.0116	
Average	0.9264	0.0088	
Pure diol	0.9514	0.0015	0.0038

b = Regression coefficient, S_b = standard error of b, S_e = standard error of estimate.

for the latter the value 0.9514 should be used. It is believed, however, that repetition with a greater number of series might show a significantly different regression coefficient for crude diol products.

For ease of computation in routine work it is desirable to use the formula: diol present = diol by analysis × correction factor. The best estimates of these correction factors are obtained by dividing the diol purity (in this case 0.9888) by the corresponding regression coefficient, and are therefore: 1.039 for pure diol solutions, and 1.067 for all other materials. From the standard errors of estimate, given in Table IV, it appears that the factors are most reliable with pure diol solutions and least reliable with syrups.

It is believed that these results can be applied to the *Aerobacter aerogenes* fermentation process also, because the products are similar.

Insoluble Solids in Mashes and Beer-still Slops

To calculate diol concentrations on the basis of fermented mash the amount of insoluble solids present must be known. The same absolute amount of insolubles may be used in connection with the corresponding beer-still slops providing no appreciable change in the distribution of soluble and insoluble solids takes place during passage through the beer still.

This problem was investigated as follows. Total solids were determined in a sample of fermented mash and soluble solids in a filtrate from this mash. A portion of the mash was then boiled at atmospheric pressure for 15 min. (= approximate retention time in beer still), under a reflux condenser to prevent loss of material from the boiling sample. The boiled mash was then cooled and filtered, and soluble solids were again determined in the filtrate. No pH adjustment was made in any of the samples. All determinations were done in duplicate, and the results for two experiments are given in Table V. These results indicate that soluble solids in the mash were slightly increased during the heating operation. In most calculations, however, the effect can be ignored since, as will be shown in the next section, it enters only into the factor, 100 − percentage of insoluble solids.

Application of Results

It has been stated already that calculation of yields and material balances on diol-containing materials of widely varying characteristics necessitates careful consideration of the basis of calculation. This is especially true when large volumes with low diol contents are involved. No difficulty is encountered in dealing with syrups, crude diol products, pure diol concentrates, beers, and filtrates since these materials are essentially one phase, i.e., no insoluble solids are present. On the other hand, fermented mashes and beer-still slops are two-phase materials and the diol (and ethanol) concentrations on a liquid basis must be converted to a basis of whole mash (or whole slops).

The calculation is simple but requires knowledge of the insoluble solids. As described above, this quantity is best found by determining the total

TABLE V

EFFECT OF 15 MIN. BOILING ON DISTRIBUTION OF SOLIDS IN WHOLE WHEAT MASH FERMENTED BY *A. polymyxa*

	Experiment 1		Experiment 2	
	Ferm. 1	Ferm. 2	Ferm. 1	Ferm. 2
Mash conc., %	13.1	14.0	14.8	14.7
Final diol, %	2.15	2.33	3.26	2.50
Final ethanol, %	1.33	1.47	0.50	1.32
	Mean diff.	Mean diff.	Mean diff.	Mean diff.
Total solids in mash before boiling, %	6.50 0.04	6.51 0.05	5.47 0.01	5.97 0.01
Soluble solids in filtrate before boiling, %	3.09 0.06	3.33 0.02	3.06 0.22	3.26 0.20
Soluble solids in filtrate after boiling, %	3.22 0.05	3.61 0.06	3.03 0.17	3.46 0.07
Av. diff.	0.05	0.04	0.13	0.09

solids in the mash and the soluble solids in the filtrate. The insoluble solids, P_i, as per cent of the mash*, are then given by the formula.

$$P_i = \frac{100\ (P_t - P_s)}{100 - P_s},$$

where P_t = per cent total solids in mash,
and P_s = per cent soluble solids in filtrate.

The per cent diol, c, in whole mash, can then be calculated from the formula

$$c = \frac{c^1}{s_1}\frac{(100 - P_i)}{100} = \frac{c^1}{s_1}\frac{(100 - P_t)}{(100 - P_s)},$$

where s_1 = specific gravity of filtrate,
and c^1 = diol concentration in grams per 100 ml. of filtrate. Use of the second form of this equation eliminates a separate calculation of P_i.
If V = total volume of mash in Imperial gallons, and s_2 = specific gravity of mash, then

$$\text{Total lb. diol} = \frac{Vs_2\,c^1}{s_1}\frac{(10)}{(100)}\frac{(100 - P_i)}{(100)}.$$

The same formulae apply to the calculation of ethanol if c^1 is taken as grams of ethanol per 100 ml. of filtrate.

For a given mash concentration and assuming normal fermentations, i.e., 90% completion or better and no contamination, s_1 and s_2 are only slightly greater than unity and their ratio varies but little from one mash to the next.

* *All percentages are by weight.*

For 15% whole wheat mash s_1 may be taken as 1.01 and s_2 as 1.02. If, for the same conditions, the limits on P_i are taken as 2.5 to 3.5% then the factor $\frac{s_2}{s_1}\frac{(100 - P_i)}{100}$ will have limits 0.985 to 0.975. For approximate calculations, the insoluble solids may be taken as 3.0% and then:—

$$\text{Total lb., diol} = \frac{V\,(1.02)}{(1.01)}\,c^1\,\frac{(10)\,(0.970)}{100} = 0.0980\,Vc^1$$

It is clear that for these conditions the insoluble solids may be considered to be unchanged in passing through the beer still, although their concentration may be altered if dilution or concentration of the mash takes place.

Acknowledgments

The authors wish to thank Dr. G. A. Adams, of the Division of Applied Biology, for his constantly helpful advice and criticism throughout this work, and Mr. E. L. Tollefson for checking the several points in the analytical method. Thanks are due also to Dr. J. W. Hopkins of the Divisional Staff, for assistance with the statistical analysis.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XV. THE OCCURRENCE OF ACETONE AS A PRODUCT OF THE *AEROBACILLUS POLYMYXA* FERMENTATION

By Dyson Rose[2]

Abstract

Considerable quantities of acetone were produced by certain strains of *Aerobacillus polymyxa* growing anaerobically in a dextrose medium. The presence of acetone was confirmed by formation of the 2,4-dinitrophenylhydrazine derivative. Carbon balances were obtained for both non-acetone-producing and acetone-producing strains of the organism; considerable quantities of several organic acids were also formed. Increased efficiency of nitrogen-aeration resulted in a marked lowering of the butanediol : ethanol ratio and probably is conducive to an increased yield of acetone.

Introduction

Donker (4) in 1926 presented evidence that the fermentation of dextrose by the organism *Aerobacillus polymyxa* led to the production of significant quantities of acetone, but earlier work in these laboratories did not support this conclusion. So far as we know, other workers have not reported the production of acetone by the organism. However, during more recent work with various strains of *A. polymyxa*, it was found that satisfactory carbon recoveries could not be obtained in all experiments if analyses were made for only the expected products. A consideration of the data obtained indicated that the substance overlooked might have been acetone, and the possible presence of this substance was therefore investigated.

Materials and Methods

The general methods and procedure of conducting the fermentations were the same as those previously described (3) except that Kluyver flasks (6) were used to provide more efficient nitrogen-aeration.

The analytical methods were largely those used by Neish (8), although some modifications were made during the course of this work. Malic acid was determined by the method of Pucher *et al.*(9), acetone by the method of Goodwin (5). All analyses were made at the close of a 96-hr. fermentation period.

Experimental Results

Various strains of *A. polymyxa* were studied but data for only two of these are presented. N.R.C. strain C2(3) was selected as representing the general type because it consistently gave 2,3-butanediol and ethanol yields approximating those commonly found in the fermentation of grain mashes (7). On

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[2] *Biochemist, Industrial Utilization Investigations.*

the other hand, strain C25 under the same conditions produced less butanediol and more ethanol, and satisfactory carbon recoveries could not be obtained by the routine analytical procedures. Although no truly intermediate strains were found among those studied, considerable variation in both types of fermentation did occur.

Fermentation Products of Strains C2(3) and C25

Yields of the various fermentation products with strains C2(3) and C25, expressed as millimoles per 100 millimoles of dextrose fermented, are shown in Table I. The carbon recoveries of 97.2 and 98.3% are considered satisfactory as no attempt was made to correct for the amount of substrate assimilated by the growing culture. The ratios of the calculated: observed carbon dioxide and hydrogen yields, and the oxidation–reduction indices, are also satisfactory.

TABLE I

FERMENTATION PRODUCTS OF TWO STRAINS OF *A. polymyxa*

Millimoles per 100 millimoles of dextrose dissimilated

Product	C2(3)	C25
Butanediol	45.5	40.6
Acetoin	2.8	0.2
Ethanol	76.7	83.2
Formic acid	1.2	2.4
Acetic acid	14.0	6.3
Lactic acid	3.2	2.9
Succinic acid	1.8	1.6
Malic acid	0.5	0.2
Carbon dioxide	188.3	200.7
Hydrogen	90.1	97.9
Acetone	Tr. (?)	9.5
Dextrose fermented	5077	5066
Carbon recovery, %	97.2	98.3
CO_2, calc./obs.	1.013	1.00
H_2, calc./obs.	0.998	1.001
O/R index	0.987	1.001
$\frac{\text{Acetoin + diol}}{\text{Ethanol}}$ (by weight)	1.23	0.96

These data differ from those of Adams and Stanier (3) in that formic, lactic, succinic, and malic acids are present in the fermented medium. The method used for estimating formic acid in the present work was more delicate than theirs, and it is not impossible that traces of formic acid were present in their medium even though high carbon recoveries were obtained. Succinic acid was obtained in all the present experiments so that strain differences would not appear to be an adequate explanation for its absence in the experiments recorded by Adams and Stanier. Wood and Werkman (12) have reported that various factors, especially the presence or absence of phosphate in the medium, affect the production of succinic acid by *Propionobacterium*, and Neish (8) has shown that differences in the culture media greatly affect

the yield of acids by *Bacillus subtilis*. No significant differences between our medium and that used by Adams and Stanier could be found and consistent changes in the amount of succinic acid formed could not be induced by minor changes in the medium. It seems probable that the formation of lactic and succinic acids is a function of the particular medium and conditions used.

In the absence of succinic acid, no tests for malic acid were made by Adams and Stanier. It is probable that the yeast extract rather than the dextrose was the source of malic acid; the amounts found were frequently less than those shown in Table I.

The acetone production shown for Strain C25 in Table I was calculated on the assumption that one mole of acetone and three moles of carbon dioxide are produced per mole of dextrose utilized, and that the ratio of calculated to observed carbon dioxide must be 1.0. If acetone is not included in the balance, the carbon recovery amounts to only 93.5%, the ratios of the calculated to observed carbon dioxide and hydrogen are 0.86 and 0.61 respectively, and the oxidation–reduction index is 1.05. Obviously such values indicate that some product has been overlooked, and the improvement that results in all these values when acetone is included, computed on the basis of the carbon dioxide found in excess of that calculated, provides strong evidence that acetone is the missing product.

Analyses for acetone were later conducted on a medium fermented by Strain C25 under similar conditions and gave clear evidence that a considerable amount of this product was being produced. Positive identification of the acetone produced in these fermentations was made by means of the melting point and mixed melting point of the 2,4-dinitrophenylhydrazine derivative.

On the other hand, the data in Table I indicate that acetone is not produced in sufficient quantity to affect the carbon balance for the C2(3) fermentation, and subsequent tests with cultures in 200-ml. flasks tended to support this conclusion, although slight positive results were obtained when analyses for acetone were made by the iodoform method. These results indicate an acetone content of about 0.01% in the fermented medium, and were greater than could be explained on the basis of the interference due to ethanol. It therefore appears probable that even with this strain of the organism traces of acetone were formed under the conditions used in these fermentations.

While the work recorded in this paper was in progress, Tollefson *et al.* (11) found that acetone could be recovered by rectification of the low boiling fraction of the medium fermented by *A. polymyxa*. This observation does not prove that acetone is produced by *A. polymyxa*, owing to the possibility that contaminated fermentations were included, but it does provide confirmatory evidence.

The Effect of Nitrogen-aeration on the Fermentation

Although the usual ratio of butanediol to ethanol obtained in anaerobic fermentations with *A. polymyxa* is about 1.3 : 1 by weight (1), values of less than 1.0 : 1.0 have been consistently obtained in fermentations that produce

significant quantities of acetone. Adams and Stanier (3) suggested that differences in this ratio are due to variations among the strains of the organism, and our experience has tended to support the suggestion. It has been found, however, that differences in the rate and efficiency of nitrogen-aeration tend to augment the effect of strain differences. Table II presents data that serve to illustrate this effect, from six experiments conducted with Strain C25 under varying degrees of nitrogen-aeration.

In some of these experiments (Method I) approximately equal amounts of nitrogen were admitted in either coarse or fine bubbles, while in others (Method II) varying amounts of nitrogen were admitted in fine bubbles. The rates of nitrogen-aeration for the latter are recorded together with the acetone yields in Table III.

The data in Table II show that increasing the degree of nitrogen-aeration by either of these methods results in a decrease in the butanediol: ethanol ratio. The differences between the means for Method I are statistically significant, indicating that coarse bubbles result in a higher butanediol: ethanol ratio as compared with fine bubbles. No significant difference was shown between the effects of slow and fast aeration.

TABLE II

THE EFFECT OF THE RATE OF NITROGEN-AERATION ON THE BUTANEDIOL : ETHANOL RATIO

Method I

Exp. no.	Coarse bubbles			Fine bubbles		
	Diol	Ethanol	Ratio	Diol	Ethanol	Ratio
1	0.302	0.278	1.09	0.230	0.264	0.87
2	.359	.254	1.41	.249	.259	.96
3	.262	.268	0.98	.141	.251	.56
Average			1.16 ± .18			0.80 ± .17

Method II

Exp. no.	Slow aeration			Fast aeration		
	Diol	Ethanol	Ratio	Diol	Ethanol	Ratio
1	0.165	0.237	0.70	0.122	0.244	0.50
2	.144	.231	.62	.120	.217	.55
3	.143	.208	.69	.122	.195	.63
Average			0.67 ± .04			0.56 ± .05

Method I:—*Kluyver flasks, coarse bubbles of nitrogen admitted through a glass tube inserted through the top of the flask; fine bubbles of nitrogen admitted through the sintered glass disk.*

Method II:—*Kluyver flasks, nitrogen admitted through the sintered glass disk at varying rates. Cf. Table III.*

The production of acetone by Strain C25 in some of these experiments is shown in Table III. The average amount of acetone found is approximately double that calculated for Table I, in which the data were obtained from a medium that was nitrogen-aerated at a rate of about 60 to 70 cc. per litre per min. The data in Table III also indicate that the yield of acetone tends to increase with increasing rates of nitrogen-aeration, but since good control of the rates of gas flow was not obtained these results are not conclusive. Since

TABLE III

THE EFFECT OF THE RATE OF NITROGEN-AERATION ON PRODUCTION OF ACETONE BY *A. polymyxa* STRAIN C25

Approx. rate of nitrogen-aeration, cc./litre/min.	Acetone, % of medium		Total
	Retained in medium	Recovered from trap*	
20	0.036	0.001	0.037
100	.045	.004	.049
50	.057	.016	.073
150	.033	.045	.078
75	.028	.035	.063
300	.024	.067	.091

**A sodium bisulphite trap was used to collect the acetone swept out by the nitrogen stream. The acetone thus caught was later released by the addition of alkali and recovered for analysis by distillation.*

increased aeration tends to remove more acetone from the medium, an attempt was made to decrease its production by the addition of acetone at the time of inoculation, but the subsequent evaporation of the added acetone obscured the results. Indications were, however, that the added acetone had no effect on the fermentation, and it seems doubtful whether the apparent effect of aeration on the acetone production can be directly due to the sweeping out of this product as it is formed.

Discussion and Conclusions

The fact that certain strains of *A. polymyxa* are capable of producing a considerable quantity of acetone is adequately proved by the data presented. The amounts of acetone obtained with Strain C25 under our conditions greatly exceed those recorded by Donker (4), and are sufficient to affect the commercial production of butanediol by means of this fermentation. However, since strains used in commercial plants would be selected for a favourable butanediol : ethanol ratio there appears to be little likelihood of acetone-producing strains being used. The low butanediol : ethanol ratio obtained in all cases where acetone was formed indicates that this product arises at the expense of the diol while the ethanol production remains relatively constant or even increases.

The significant effects exerted by the rate and efficiency of nitrogen-aeration on the butanediol : ethanol ratio, and probably on the acetone production, are of considerable interest. The most probable explanation is that some product of the fermentation reactions is removed from the medium by the gas stream. The data available do not favour the conclusion that the product thus being removed is the acetone itself. Adams (1) and Adams and Leslie (2) have shown that the removal of carbon dioxide from the fermenting medium has a marked effect on the fermentation. It is significant, however, that under conditions of excess aeration with nitrogen, in spite of the decreased diol production, no increase in ethanol or any other product whose precursor acts as an hydrogen acceptor is evident. This is in contrast to the strain differences noted in Table I and would seem to indicate that hydrogen is being rapidly swept from the medium instead of being used to reduce some intermediary product. The formation of acetone from pyruvate through acetic and acetoacetic acids involves the removal of hydrogen as well as carbon dioxide, and the fate of this hydrogen is not known. It seems possible that the increased formation of acetone under conditions of efficient nitrogen-aeration may be at least partly due to the increased removal of gaseous hydrogen from the medium.

The ability of *Aerobacillus* strains to produce variants, and the need for constant selection if a parent strain is to be kept pure, is well known. It is worth noting, however, that the acetone-producing strain used in these experiments (C25) is a descendant of the organism used by Adams and Stanier (3). From time to time during the intervening two years this organism has been plated out and any variants differing morphologically from the original were eliminated. In spite of this repeated selection the fermentation induced by the strain now bears little resemblance to that of the parent culture, and it seems unlikely that this is entirely due either to differences in the medium used or to the increased efficiency of nitrogen-aeration. The conclusion that considerable physiological variation has occurred without noticeable variation in morphological form seems inescapable and the necessity for frequent testing of strains is thus distinctly emphasized.

Acknowledgment

The author wishes to express sincere thanks to the Department of Biochemistry, University of Toronto, for the facilities provided during part of this investigation.

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DRIED WHOLE EGG POWDER

XXI. PASTEURIZATION OF LIQUID EGG AND ITS EFFECT ON QUALITY OF THE POWDER[1]

By N. E. Gibbons[2], C. O. Fulton[3], and Margaret Reid[4]

Abstract

Heating liquid egg to 60°C. reduced the viable bacterial count 85 to 95% but had less effect on the coliform organisms. Holding the liquid at 60°C. for 30 min. reduced the viable count 98 to 99%, and destroyed the coliforms, *Salmonella*, and *Staphylococci*. Quality tests indicated no difference between powders prepared from heated and unheated melange either originally or after storage. Tests with a laboratory flash pasteurizer indicated that a considerable reduction in the number of total viable and coliform organisms occurred when liquid egg was heated from 22° to 60°C., the total time in the pasteurizer being approximately one minute.

Introduction

The presence of organisms of the *Salmonella* group (4) and coagulase positive *Staphylococci** in dried egg powder introduced a public health hazard that at one time was viewed with some alarm. Previous studies indicated that in the interests of quality the temperature of drying should be as low as possible and the powder should be cooled as rapidly as possible (12). Both of these recommendations favoured the survival of bacteria during the drying process (3). The present studies were undertaken to determine the feasibility of destroying possible pathogens by heat treating liquid egg and to evaluate the effect of this treatment on the keeping quality of the powder.

Although the principle of heating liquid egg to facilitate drying was well known, little information was available on the heat treatment of liquid egg with the object of destroying bacteria. It has been stated that broken out duck eggs may be pasteurized by adding sodium citrate, heating to 65°C. for 20 min., and cooling rapidly (10). In a criticism of this method it was claimed that the heating period of 20 min. was not always sufficient to kill *Salmonella* (11). Recently some work on hens' egg melange has been done in the United States (5).†

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* *Unpublished data.*

† *Since this paper was submitted, this work has begun to appear in more detail.*

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Materials and Processing Methods

Preliminary tests indicated that fresh egg liquid could be heated to 52° and 59°C. (126° to 138°F.) for periods up to 12 hr., with a reduction in the bacterial content, but without affecting the fluorescence value of the powder prepared from it. Fresh melange could be heated to 66°C. (151°F.) and held 30 min. with no evidence of coagulation, provided it was stirred vigorously. There was some coagulation when the temperature was raised to 68°C. (154°F.). It was not possible to obtain these temperatures in the commercial trials with the equipment available as the temperature differentials necessary were so high that coagulation occurred on the heating coils; the highest practical temperature was 60°C. (140°F.).

Liquid egg was divided into two portions, one of which was inoculated with *Escherichia coli*, and the other with an organism resembling *Streptococcus faecalis*. Portions of each lot were heated in 5 to 10 min. to 55°, 57°, and 60°C. (131°, 135.5°, and 140°F.). After one-half, one, two, three, and four hours, samples were removed for bacteriological analysis and for drying. The samples for drying (100 ml.) were frozen immediately at −40°C. and dried in a vacuum over calcium chloride as soon as possible. The powders were stored at −40°C. until all had been prepared. Fluorescence and potassium chloride were then determined and the powder stored 21 days at 37°C. when the fluorescence was again measured.

Based on the results of these tests, further experiments were made with mixtures of *E. coli*, *E. freundii*, and *Aerobacter aerogenes*, of *Salmonella*, and of hemolytic *Staphylococci* and *Streptococci*.

For the first commercial trial, 2000 lb. of liquid egg prepared from frozen blocks was used. The drier and all tanks and lines had been cleaned some hours previously and filled with hypochlorite solutions and rinsed with hot water. The melange was heated to 60°C. in a cream forewarmer, consisting of an open uninsulated metal tank with a rotating helix through which hot water was circulated at 82°C. (180°F.). The mass was heated from 8° to 60°C. in 54 min. This time could probably have been shortened but the temperature at which the egg might coagulate on the coils was not known. After holding the liquid 30 min. at a temperature of 59° to 60°C., it was pumped into an insulated holding tank and fed as needed through a line filter into a small ballast tank near the drier. All of the liquid was dried 2.5 hr. after pasteurizing. The temperature of the melange and outlet air temperature of the drier are given in Fig. 1. Samples of powder were collected 10, 85, and 145 min. after drying began and immediately cooled. As soon as the heated egg was dried, the drying of unheated liquid from the same master batch was resumed and after 30 min. of operation a sample of powder was collected as a control. All samples were analysed bacteriologically and chemically at once and after storage for three weeks at 37°C.

In a second trial, five lots of 2000 lb. each were processed. The melange was prepared the day before, cooled, and held at 4°C. (39°F.) overnight. The

holding temperatures and times are given in Table III. Lot *B* was raised to temperature more rapidly than *A*. The control powder (*F*) was prepared from the same master batch of melange immediately after the others were dried. Throughout the trials the temperature of the water entering the coils

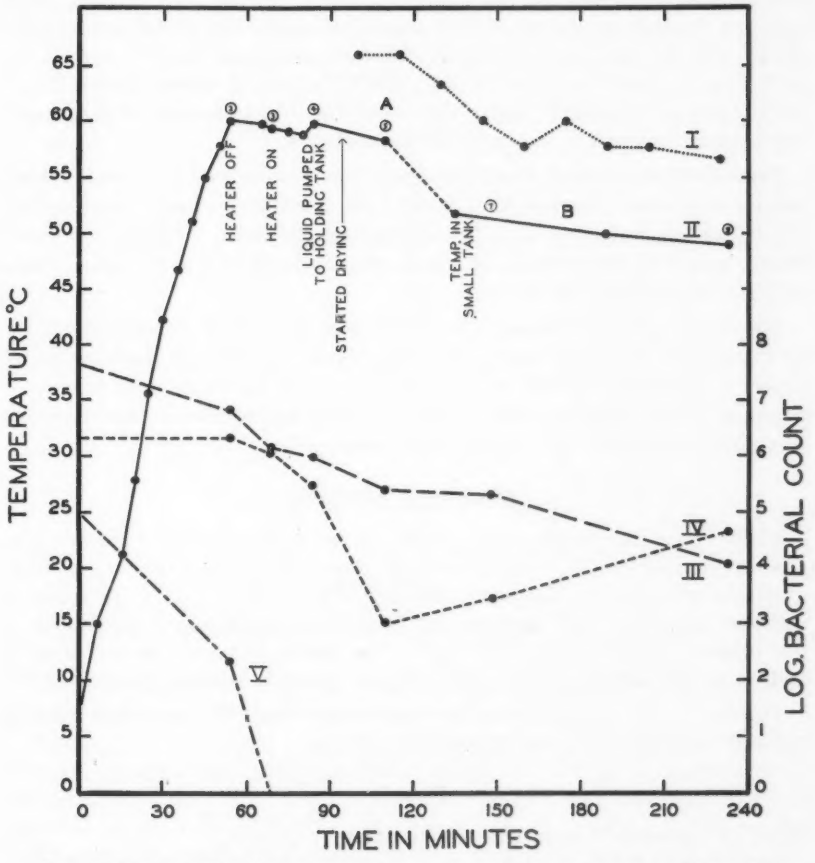

FIG. 1. *Data regarding first commercial run. I—outlet air temperature of drier; II—temperature of liquid egg; III—viable bacterial count at 37°C.; IV—viable bacterial count at 55°C.; V—coliform content; 1, 2, etc.—samples of liquid egg taken; A, B—samples of powder taken.*

was between 81° and 86°C. (178° to 187°F.). The air inlet temperature to the drier was 96°C.; the outlet temperature varied between 57° and 60°C. On leaving the drier the powder was cooled in a ramshorn with air at 5°C. Approximately 10 lb. from the first of each run was excluded from the test material. Samples for analysis were taken as the powder was being sifted into barrels.

Between lots, all lines and tanks, with the exception of the ballast tank, were washed with hot water and steam. The ballast tank was merely washed with hot water to allow continuous operation of the drier.

The powder was stored at 16°C. (60°F.) and packaged after five days. At that time 14 lb. of test material was removed from each lot by taking small amounts throughout the packaging operation. This was stored at −1.1°C. (30°F.) for six days, then sealed in cans and stored at 32.2°C. (90°F.) for periods up to four weeks, at 26.7°C. (80°F.) up to 12 weeks, and at 21.1° (70°F.) and 15.6°C. (60°F.) up to eight months. The remainder of the powder was shipped overseas in the usual 14-lb. packages.

Since there are several disadvantages to vat pasteurization, a small experimental unit was constructed to explore the possibility of flash pasteurizing the liquid egg immediately before it entered the drier. Three glass tubes 80 cm. long with inside diam. of 3 mm. were enclosed in a water jacket made of glass tubing (41 mm. I.D.).

Water was pumped through the jacket from a constant temperature bath by means of a centrifugal pump. The egg was forced through the tubes (total capacity approximately 17 ml.) at the rate of about 20 ml. per min. by a constant volume delivery pump. Some liquid egg pasteurized in this apparatus was pumped directly into a laboratory spray drier (14).

Analytical Methods

Viable bacterial counts were made on proteose-peptone–tryptone agar after incubating at 37°C. (98°F.) for three days. In the first commercial trial, duplicate plates were also incubated at 55°C. (131°F.). The presence of coliform organisms was detected by inoculating appropriate dilutions into five tubes of brilliant-green bile broth. Gas production was checked after 24 and 48 hr. incubation at 37°C. and the most probable number determined (1).

Powder quality was evaluated by fluorescence value (8), potassium chloride value (9), moisture (9), and palatability (8).

Results

Effect of Pasteurization on Bacterial Content

The results of several preliminary experiments are summarized in Table I. At 60°C. the viable count reached a minimum and all coliforms had been killed in 30 min. At 57.5°C. this was not accomplished for at least three hours. Mixtures of at least two strains each of *E. coli*, *E. freundii*, and *A. aerogenes* and of five types of *Salmonella* were destroyed in 25 min. at 60°C. Six strains of α-toxin producing, coagulase-positive *Staphylococci* were killed in 15 min. at 60°C. and four strains of Group A *Streptococci* were killed in 10 min. at 60°C., although 20 min. was taken to attain the desired temperature. It would seem therefore that 60°C. for 30 min. is the shortest time possible for vat pasteurization.

TABLE I

EFFECT OF HEATING LIQUID EGG ON THE BACTERIAL CONTENT

Organism added	Approx. time to attain pasteurization temp., min.	Pasteurization temp., °C.	Holding time at pasteurization temp., min.	Log. no. organisms per ml.			
				Initial		After heating	
				Viable	Coliform M.P.N.†	Viable	Coliform M.P.N.
*E. coli**	8	60	15	7.57	6.25	4.00	0.30
			30			3.45	0
			60			3.34	0
	5	57.5	30	7.73	7.85	4.22	1.34
			60			3.63	1.23
			120			3.48	1.34
			240			3.30	.30
	5	55.0	30	7.85	6.25	5.74	3.30
			120			4.04	2.20
			240			3.59	2.26
*E. coli*** *E. freundii* *A. ærogenes*	4	60	10	7.13		3.73	
			20			1.18	
			25			0	
Salmonella spp.**	4	60	10	7.26		3.04	
			20			1.70	
			25			0	
*Staphylococci*** α-toxin, coagulase +	20	60	0	7.50		2.60	
			15			0	
*Streptococci*** Group A	20	60	10	6.90		0	
*S. faecalis**	10	60	30	4.70		3.45	
			60			3.41	
			120			3.32	

†*M.P.N.—Most probable number of organisms.*
**Added to melange containing other organisms.*
***Added to melange containing < 10 other organisms per ml.*

The first commercial trial was based on these results. The pertinent data and the decrease in bacterial content are shown in Fig. 1.

The high initial viable count was attributed to thawing frozen melange with warm water and failing to cool it promptly. It served admirably for the purpose of the test. The viable count at 37°C. had decreased to about one-sixth of the original by the time the temperature of the liquid reached 60°C. and at the end of the 30 min. holding time there was a 98% reduction. The reduction in count continued in the liquid awaiting drying, and at the final sampling was 99.97%.

The number of coliform organisms decreased from 92,000 per ml. initially to 220 per ml. by the time the temperature of the liquid had reached 60°C., and none could be detected in 10-ml. amounts after 15 min. heating.

Organisms capable of growing on plates incubated at 55°C. were reduced to only 15% of the original number at the end of the pasteurizing period. The number continued to decrease for a short time afterwards, but as the temperature of the melange approached 55°C. began to increase again. Since none

of these organisms is pathogenic, they are of little significance. However, their behaviour serves to point out some of the dangers inherent in batch processes and to emphasize the fact that the liquid should be dried as rapidly as possible after heating.

The powder prepared from the pasteurized liquid contained only a small fraction of the number of viable bacteria present in that prepared from untreated egg (Table II).

TABLE II

QUALITY MEASUREMENTS AND BACTERIAL CONTENT OF POWDERS PRODUCED FROM PASTEURIZED AND UNPASTEURIZED LIQUID EGG (FIRST COMMERCIAL TRIAL)

	Moisture %	Fluorescence value		Palatability ratings	Potassium chloride value	Viable bacterial count, log. no. per gm.	
		Initial	After 3 weeks at 37°C.			37°C.	32°C.
Pasteurized*							
G	2.77	13.5	43.3	7.5	68.2	4.71	4.82
H	3.05	14.0	42.7	8.0	72.5	4.64	4.62
I	2.80	15.0	40.0	8.5	70.5	4.54	4.58
J Unpasteurized	4.16	14.0	46.4	8.5	73.1	6.88	6.93

**Collected 10, 85, and 145 min. respectively after drying began.*

TABLE III

EXPERIMENTAL DATA ON SECOND COMMERCIAL PASTEURIZATION EXPERIMENT

Lot	Holding temp., °C.	Time to attain temperature, min.	Holding time, min.	Moisture content of powder, %
A	60	69	30	3.75
B	60	36	27	3.60
C	60	48	0	3.68
D	57	36	10	4.02
E	57	64	0	4.16
F (control)	—	—	—	3.77

In the second commercial trial the heating-up period was the most destructive to the bacterial population, but within the limits studied the time taken to reach temperature had little effect (Table IV). The time of holding had little effect on the final number of organisms. The temperature attained was most important in determining the viable count in the liquid.

The heating-up period (Table IV) was as destructive to the bacteria as the whole pasteurizing period in the previous experiment (Table II). In the

control powder (*F*) the percentage reduction due to drying alone was as great as that obtained by both pasteurizing and drying. Although such high percentage reductions due to drying alone have been reported (7), they are not usual (2 ,3) and the extent of reduction probably depends on the particular flora of the melange being dried. The data for coliform organisms are unfortunately not complete; nevertheless, the indications are that at these temperatures a holding period is necessary to eliminate these organisms from the melange (Table IV). The high coliform content of the powder produced

TABLE IV

LOGARITHM OF NUMBER OF VIABLE ORGANISMS GROWING AT 37°C. AND OF MOST PROBABLE NUMBER OF COLIFORMS AND *E. coli* IN EGG MELANGE AND POWDER IN SECOND COMMERCIAL EXPERIMENT

Sample*	Log. viable count, 37°C.					
	*A***	*B*	*C*	*D*	*E*	*F*
1	6.39	6.53	6.60	6.28	6.83	—
2	4.56	4.46	4.47	4.98	4.93	—
3	4.34	4.43	—	4.70	—	—
4	4.26	4.14	4.24	4.57	4.60	—
5	4.79	4.82	4.99	5.20	5.31	5.17
	Coliforms			*E. coli*		
	A	*C*	*E*	*A*	*C*	*E*
1	4.29	—	4.59	3.99	—	4.08
2	—	2.10	2.54	—	2.10	2.41
3	1.78	—	—	1.54	—	—
4	—	—	1.75	—	—	1.08
5	2.02	0	0.48	1.34	—	0

**Sample 1—before heating, 2—on reaching temperature, 3—at end of holding period, 4—from ballast tank, 5—powder.*

***For treatment see Table III.*

from the first run (*A*) was no doubt caused by contamination. Later tests indicated that the high pressure pump may have been the source of this contamination.

The results of the initial experiments with the flash pasteurizer are shown in Table V. By appropriately adjusting the temperature of the water jacket, the temperature of the effluent egg was varied by one-degree intervals between 55 and 62° C. The original melange contained 625,000 organisms per ml. and, with 1-ml. amounts, 10 of ten tubes were positive for coliform organisms. The initial temperature was 20° to 22°C. A 99% reduction in the viable count was accomplished with an effluent temperature of 57°C. and the reduction increased as the temperature increased. With the dilutions used, little information was obtained about the reduction in numbers of coliform

organisms; no reduction was apparent until a temperature of 62°C. was reached. However, the liquid egg leaving the pasteurizer at 61°C. was slightly thick, so 60°C. was regarded as the highest working temperature with this equipment.

TABLE V

EFFECT OF TEMPERATURE ON BACTERIAL CONTENT OF FLASH PASTEURIZED MELANGE

Temp. egg at outlet, °C.	Viable count, no. per ml.	Coliform: no. of 10 tubes positive
55	2600	10
56	22,000	10
57	1300	10
58	590	10
59	750	10
60	150	10
61	50	9
62	25	1
Original melange	625,000	10

In a later trial the pasteurizer was set up in conjunction with the laboratory spray drier and three lots of powder dried (Table VI). Lot *K* was put through the pasteurizer, cooled immediately, and later put through the drier. Lot *L* was pasteurized and pumped directly into the drier without cooling. Lot *M*

TABLE VI

EFFECT OF FLASH PASTEURIZATION ON THE BACTERIAL CONTENT OF EGG POWDER AND ON THE QUALITY INITIALLY AND AFTER STORAGE FOR THREE WEEKS AT 37°C.

Lot*	Viable count, gm.	*Coli*, M.P.N./ gm.	Moisture, %	Fluorescence values		Potassium chloride value		Palatability
				Initial	After storage	Initial	After storage	Initial
K	10,000	1000	2.63	21.9	50.9	65.0	40.0	7.8
L	8000	0	2.25	21.5	52.0	71.0	43.0	8.8
M	34,000	5000	3.98	22.0	60.6	64.6	38.0	8.3

**See text for treatments.*

(control) was put through the cold pasteurizer. In lots *K* and *L* the water jacket was maintained at a temperature of 62.5°C. and the egg liquid at the outlet ranged from 59.5° to 60°C.

The original melange contained 1,700,000 organisms per ml. The melange of lot *K* had a viable count of 140,000 per ml. after pasteurization (92% reduction). The data on the powders (Table VI) indicated that pasteurization

followed immediately by drying (lot *L*) is more effective than cooling the pasteurized liquid and drying later. However, the results are not conclusive and further work is necessary with more efficient heat exchangers.

Effect of Pasteurization on Powder Quality

The early experiments indicated that heating liquid egg for periods up to four hours did not increase the development of fluorescence during storage of the resulting powder (Table VII); the indications were that the longer heating periods retarded the development of fluorescence.

TABLE VII

EFFECT OF STORAGE FOR 21 DAYS AT 37°C. ON FLUORESCENCE VALUES OF POWDER PREPARED FROM UNHEATED AND HEATED LIQUID

Holding time, hr.	Fluorescence values	
	Initial	After storage
0	12.5*	29.8*
0.5	11.9	28.8
1	11.9	29.2
2	12.1	28.7
3	12.1	26.6
4	11.8	25.0
Necessary difference	1.1	2.7

**Means of three trials at 55°, 57.5°, and 60°C. The difference between them was not significant. Moisture content of all powders, 2.58 ± 0.10%.*

In the first commercial trial no significant differences between the powder prepared from treated and untreated melange could be detected initially by any of the measures of quality used (Table II). After storage at 36.7°C. for periods up to three weeks the fluorescence values of the pasteurized material were slightly less than those of the controls (Table II). This was attributed in part to the higher moisture content of the latter (13). As in the early experiment, there was an indication that the longer the liquid was kept hot the slower the development of fluorescence. This possibly indicates a destruction of enzymes.

The lower moisture content of the powder prepared from the heated melange is interesting. As may be seen from Fig. 1 the air outlet temperature was very high at the beginning owing to inexperience in drying hot liquid. It was necessary to reduce the heat input into the incoming air by one-half to bring the outlet temperature to the usual 135°F. As the same nozzle and the same pump pressure (2800 lb. per sq. in.) were used, no difference was observed in the amount of powder dried.

The moisture contents of the powder prepared in the second commercial trial were more comparable (Table III). The changes in fluorescence and potassium chloride values during storage at 32.2°, 26.7°, 21.1°, and 15.0°C.

of powders prepared from pasteurized melange and the control powder are shown in Fig. 2. Fluorescence measurements showed no difference between the treated and untreated material. Although average values only are shown in the figures, the potassium chloride values of the powders from unheated egg and that heated to 57°C. were slightly higher than those from egg heated to 60°C. This difference was apparent during most of the storage period but was not always noticeable at the end.

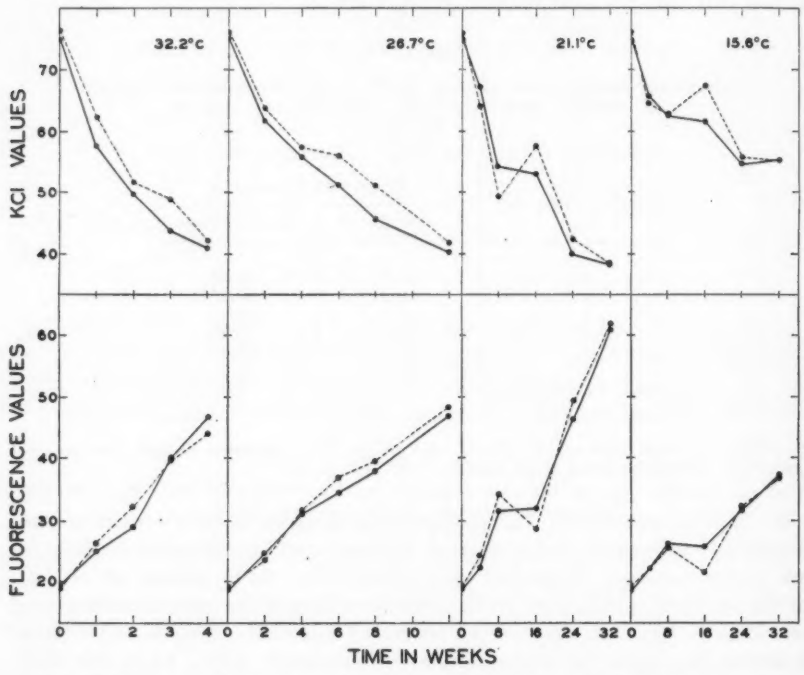

FIG. 2. *Changes in fluorescence and potassium chloride values of pasteurized and unpasteurized egg powders on storage. Treatment of liquid egg as in Table III. Solid line—unheated liquid. Broken line—mean value for five lots of powder from pasteurized liquid.*

The powder shipped overseas was tested there by a number of other tests (Haenni solubility, foam volume, creaming, flavour, and pH), with insignificant differences between the pasteurized powders and the control (6). It was remarked that the pasteurized powder was caked to some degree and resembled material that had been lightly compressed and then crumbled. This had been noted when packing the material but the lumps were easily broken up.

Samples of lots *A* and *F* were stored overseas at 37°C. for 10 weeks with no difference between the two in flavour, foam volume, creaming, and Haenni solubility.

With the exception therefore of a tendency to pack and a slightly lower solubility there was little or no difference in the original and keeping properties of egg powders prepared from untreated and vat pasteurized melange.

Panels of six persons passed judgment on scrambles prepared from all of the powders of the second commercial experiment before and after storage. Considering the variation between persons, there was little or no difference in the ratings given the pasteurized powders as compared with the controls. Treated and untreated powders deteriorated at practically the same rate.

The results of the initial quality tests on the powders prepared with the flash pasteurizer are shown in Table VI. There was little difference between the control (lot *M*) and the treated material. The deterioration during storage at 37°C. for three weeks was practically the same for all three powders, considering the higher moisture content of the control.

Commercial apparatus for flash pasteurization was not available for further work. However, such apparatus operating with lower temperature differentials and more turbulent flow might allow higher temperatures to be used without coagulation. Regulating the flow to drier capacity would eliminate the accumulation and holding of hot liquid, and conserve the heat introduced into the liquid.

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OIL CONCENTRATION BY THE FROTH FLOTATION OF PEBBLE-MILLED SEED[1]

By N. H. Grace[2] and J. B. Palmer[3]

Abstract

Froth flotation of water-cooked pebble-milled milkweed seed or mustard screenings yielded 90% of the total oil in the concentrate, which was enriched to twice the oil content of the original seed. Protein and inorganic matter also tended to concentrate in the froth fraction. Optimum conditions for separation required pH values substantially below 7 and pulp densities between 2 and 5%. Iodine numbers of oil and ease of protein peptization differed for concentrate and tailing fractions, showing some fractionation as well as concentration.

Introduction

The recent application of froth flotation to the separation of resin–rubber from milkweed leaves (5, 8, 9) suggested the further use of this method of separation or concentration of other materials occurring in plants. Seed of relatively low oil content has been selected as a plant material possibly amenable to processing with the pebble mill and flotation cell. The industrial utilization of oil from large tonnages of material such as grain screenings might be furthered by the application of comparatively low-cost methods of grinding and separating oil. This communication describes the results of preliminary experiments on the application of froth flotation to pebble-milled aqueous seed pulps. Study of the distribution of oil effected by flotation was the main object of the investigation, but some observations were also made on the distribution of protein and inorganic matter.

Materials and Methods

Seeds used were those of the common milkweed, *Asclepias syriaca* L., and screenings, largely of seeds of mustard species, family Cruciferae. Pulp was prepared for flotation by grinding one part by weight of air-dry seed (moisture content 7 to 8%) with approximately 15 parts by weight of tap water in a porcelain-lined pebble mill charged with flint pebbles. Most of the work involved cooking the seed in about 10 volumes of boiling water for a period of one hour, draining off the aqueous liquor, rinsing the drained seed with water, and then pebble-milling. A satisfactory milling period was 15 hr. with one-gallon mills, charged with 100 gm. of seed, while seven hours in a mill of 14 gal. capacity and proportionately charged, yielded pulp with approximately equal frothing characteristics. The pebble mills were drained and rinsed to remove all solid matter, and the pulp was stirred while samples

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were removed for flotation. Pulp was subjected to flotation immediately at the close of the milling period, except in one series of experiments with milkweed in which the milled pulp was held overnight.

All flotations were made in a Fagergren laboratory sub-aeration unit using a charge of 2250 ml. of pulp. Flotation at various pulp densities involved dilution of the suspensions with tap water; a range of pH values was attained by addition of sodium hydroxide or sulphuric acid. The suspension was agitated for a period of two minutes at room temperature (about 20° C.) prior to aeration. Termination of the flotation could be judged by the increase in bubble size, the usual period being from three to four minutes. No flotation reagents were added, since the pulp contains its own frothing and collecting reagents. The concentrates (fraction carried over by froth) and tailings (residual material) were rinsed into bottles with a minimum amount of water. Samples of the feed (pulp fed to float cell) also were preserved for analysis.

The bottled suspensions of feeds, concentrates, and tailings were then centrifuged in 250-ml. wide-mouth tubes at approximately 2000 r.p.m. The liquors were usually clear, though recentrifuging was required at some of the higher pH levels. The cakes were dried *in vacuo* at a temperature no higher than 40° C., and ground in a Wylie mill. Total dry weights were recorded and samples of about 5 gm. subjected to extraction in a Soxhlet apparatus with petroleum ether (b.p. 30 to 60° C.) for a period of 24 hr. Determination of the weights of oil from cake or ground seeds permitted calculation of oil contents.

All analytical data are presented on a moisture-free basis. Protein (% Kjeldahl nitrogen × 6.25) and ash percentages are based on the weight of oil-free cake. Pulp densities are referred to dry weight of water-extracted seed. The pH values are given as recorded by a Coleman glass electrode. Iodine numbers (Wijs) were determined for a few of the mustard oil samples. The nitrogenous constituents of a few samples of solvent-extracted mustard meal were peptized by a recently described procedure (4).

Data are given in graphical form for the per cent of oil, protein, or inorganic matter in both concentrates and tailings. Similar data are given for distribution to the concentrates, expressed as a percentage of the total amount of material, e.g., oil, obtained from both fractions.

Analyses of Seed and Pulps

The oil contents of these milkweed seeds and mustard screenings were, respectively, 22.3 and 21.8%. Water digestion prior to pebble-milling removed approximately 15% of water-soluble materials. The oil contents of this water-extracted seed for both milkweed and mustard were of the order of 25 to 26%.

Attainment of analytical balance of total solids and oil was an obvious prerequisite of any study of flotation. While the pebble-milling operation was effective in grinding, it tended to emulsify a part of the finely ground material. It was found that solid matter from centrifuged feed samples had

oil contents closely approximating those of the water-extracted seed before pebble-milling. However, if the prepared pulp was held for several hours between the end of the grinding operation and the beginning of flotation, the oil content of feed samples tended to be a little greater, owing, apparently, to the gradual solution of part of the material. Centrifuging of feed samples, over a range of solid contents of from 1 to 5%, recovered from 90 to 98% of both total solids and oil. Recovery approximated 100% at low pH values but fell to about 90% at pH values substantially above 7.

The violent agitation of pulps in the flotation cell might be expected to effect further emulsification and render subsequent centrifugal separation of solids and oil difficult. Consequently, the effects of pulp density and pH on recovery after flotation were investigated. The amounts of solid and oil from concentrates and tailings were obtained separately, but the combined values were expressed as percentages of the amounts recovered from feed samples.

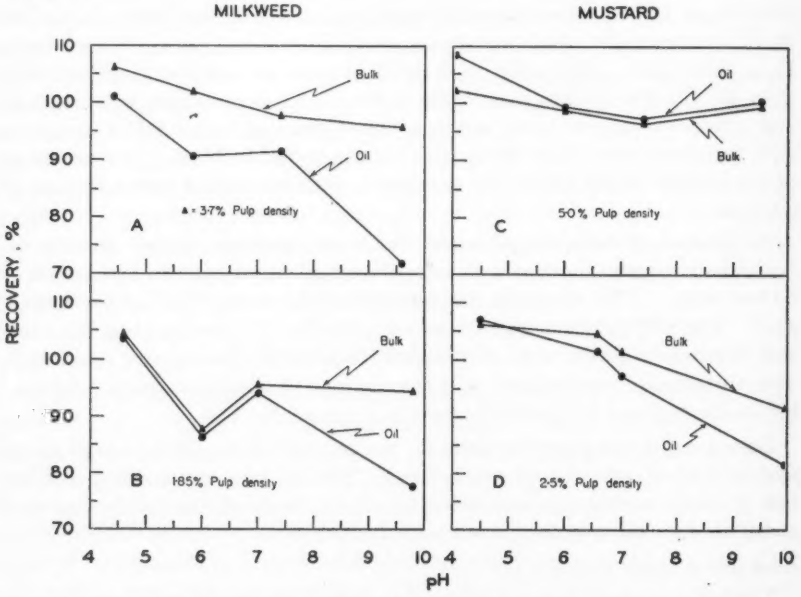

FIG. 1. *Recovery of bulk and oil after flotation at different pH levels as a percentage of recovery from feed. (Milkweed and mustard feeds, respectively, at pH levels of 5.8 and 6.0.)*

The graphs in Fig. 1 show the effects of pH on recovery of total solids and oil from milkweed and mustard seed, each at two pulp densities. Since milkweed and mustard seed when pebble-milled in tap water yield pulps with pH values of 5.8 and 6.0, respectively, these were the pulps chosen as reference feed samples. Recoveries of above 100% are accounted for by the greater efficiency of centrifugal separation in the pH range around 4 as compared

with recoveries from feed samples at pH 5.8 to 6.0. It is apparent that pH has a pronounced effect on recovery. The disadvantageous effects of high pH are more marked at lower pulp densities and on the oil fraction. Oil recovery does not fall to 90% over the entire pH range for mustard with pulp density of 5% (Fig. 1,*C*). Reduced recovery is indicated in the isoelectric region for milkweed (Fig. 1,*B*). These results show that oil recovery of about 100% is attained for pulps floated at pH values of 5 or less.

The effects of milkweed seed pulp density at pH about 5.8 on recovery from concentrates and tailings as a per cent of feed at the same pH and density are described in Fig. 2. The violent agitation of flotation of pulp with density of 6% is followed by better recovery than for the feed. Recovery increased approximately linearly with increasing pulp density; oil recovery showed more sensitive response than bulk throughout.

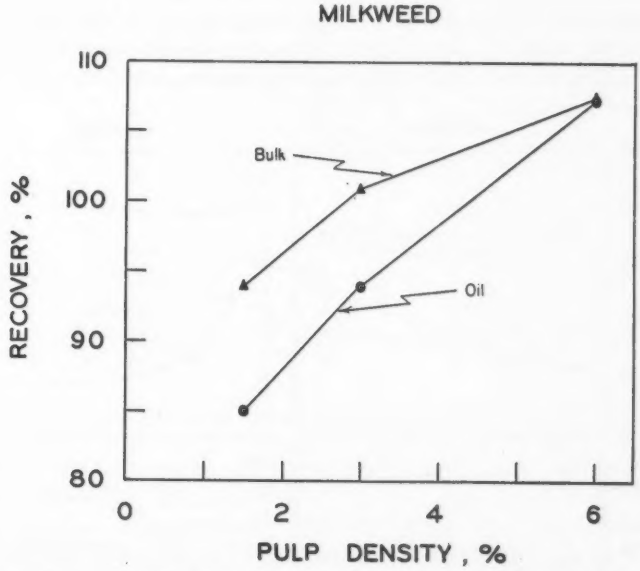

FIG. 2. *Recovery of bulk and oil after flotation at different pulp densities as a percentage of feed under corresponding conditions (pH approximately 5.8).*

It is apparent from these results that the analytical procedure yields recoveries that closely approach 100% either in the pH range below 5 or at pulp densities above 5%. In view of these findings, further refinement of analytical methods for this preliminary investigation was not deemed warranted. However, it must be recognized that the following results on flotation at either high pH values or low pulp densities are based on recovery of somewhat less than 100% of the material initially present.

Results

Frothing Characteristics

Pulps prepared from raw milkweed and mustard seed frothed voluminously, with resulting poor separation; pulps from seed previously cooked in water frothed less and showed appreciable concentration of oil in the froth fraction. Consequently, only a few preliminary observations were made on raw seed and the main investigation was confined to seed that had been cooked in water. Both pulp density and pH affected the frothing characteristics. Under favourable conditions numerous small, heavily laden bubbles were formed and the froth was wet. Froth became excessively watery under alkaline conditions; appreciably better frothing was noted with acid pulps. The frothing behaviour was quite similar to that of milkweed and other leaf tissue (9).

Effects of Pulp Density

The effects of froth flotation on oil content and distribution of oil for milkweed and mustard seed pulps with pH values of 5.4 to 5.8 but over a range of pulp densities are shown in Fig. 3. The oil content of the concentrate varied little over the range of pulp density. However, the oil contents of milkweed tailings tended to rise with increasing pulp density, while those of mustard

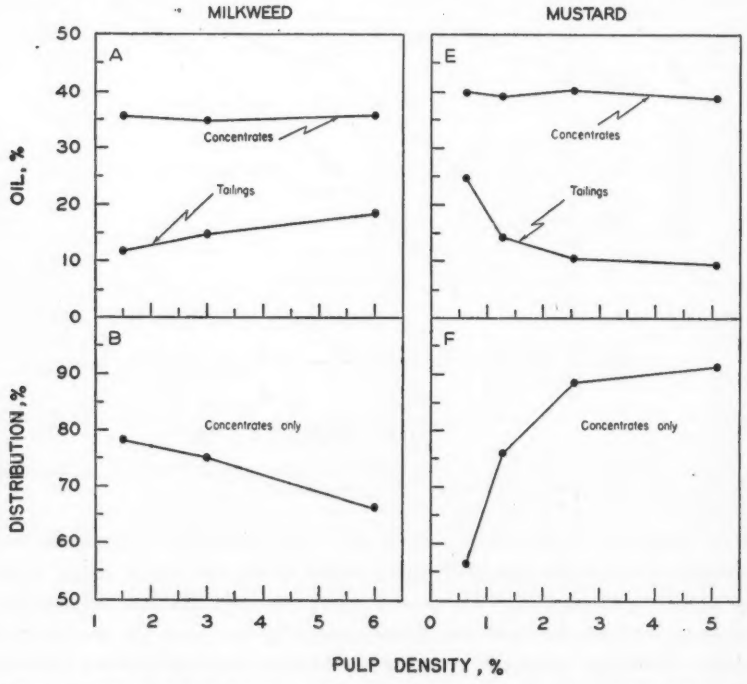

FIG. 3. *Effects of pulp density at pH approximately 5.6 on content and distribution of oil following froth flotation.*

fell rapidly and became constant. A similar tendency was noted for oil distribution in the concentrates, milkweed showing a greater percentage at low pulp densities and mustard at high. It is apparent that substantial concentration of oil occurred in the fraction carried over by the froth.

Effects of pH

In Fig. 4, *C*, *D*, are described the effects of pH on oil content and distribution of oil for milkweed. There was substantial oil concentration over the whole

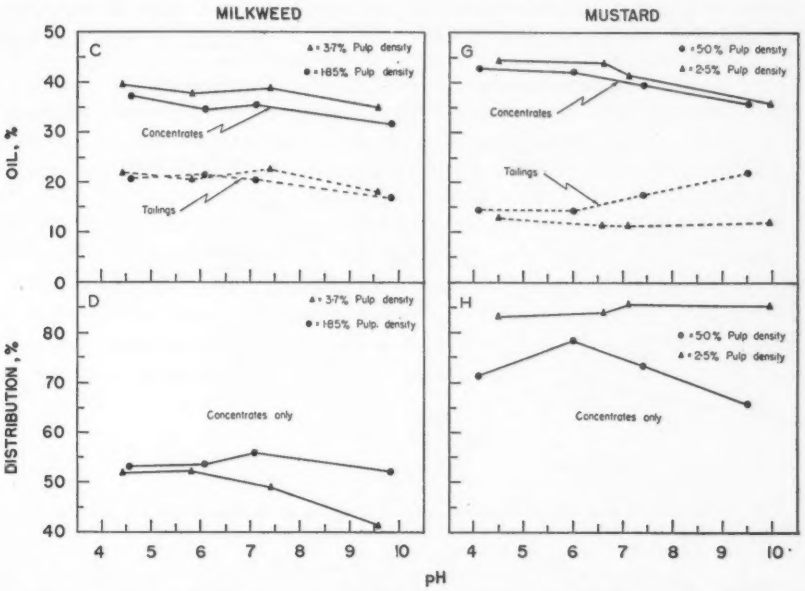

FIG. 4. *Effects of pH levels on content and distribution of oil following froth flotation.*

pH range. The oil content at 3.7% pulp density was fairly uniform but slightly greater than for pulps of one-half this density. The oil content of the tailings was approximately equal throughout for both densities. The relatively high oil contents of these tailings (compare with Fig. 3, *A*) may be attributed to the fact that the pebble-milled pulp stood overnight between milling and flotation, after which the oil contents of feed samples approximated 30% instead of the usual value of 26%. It may be seen from Fig. 4, *D* that the concentrates contained from 50 to 60% of the total oil for pulps of 1.85% solids, with a decline indicated at high pH values. This decline was accentuated with increasing pH for the pulp of greater density.

The oil content and distribution for mustard seed pulps are shown in Fig. 4, *G*, *H*. It is apparent that the results are similar to those described for milkweed though a much higher percentage of the total oil is found in the concentrates. It is, however, of interest to note the approximate linearity

of the curve for distribution of oil in the concentrates at 2.5% solids, also the tendency towards convergence at high pH values for the curves describing oil content of concentrates and tailings.

Distribution of Inorganic Matter

The ash from water-extracted mustard screenings amounted to 7.04%; that recovered from the pebble-milled pulp was 16.5%. This substantial increase in ash content resulted from attrition of pebbles and mill-linings. The effects of flotation on ash content and distribution over a range of pH values are described by the graphs of Fig. 5, *A*, *B*. It is apparent that the froth

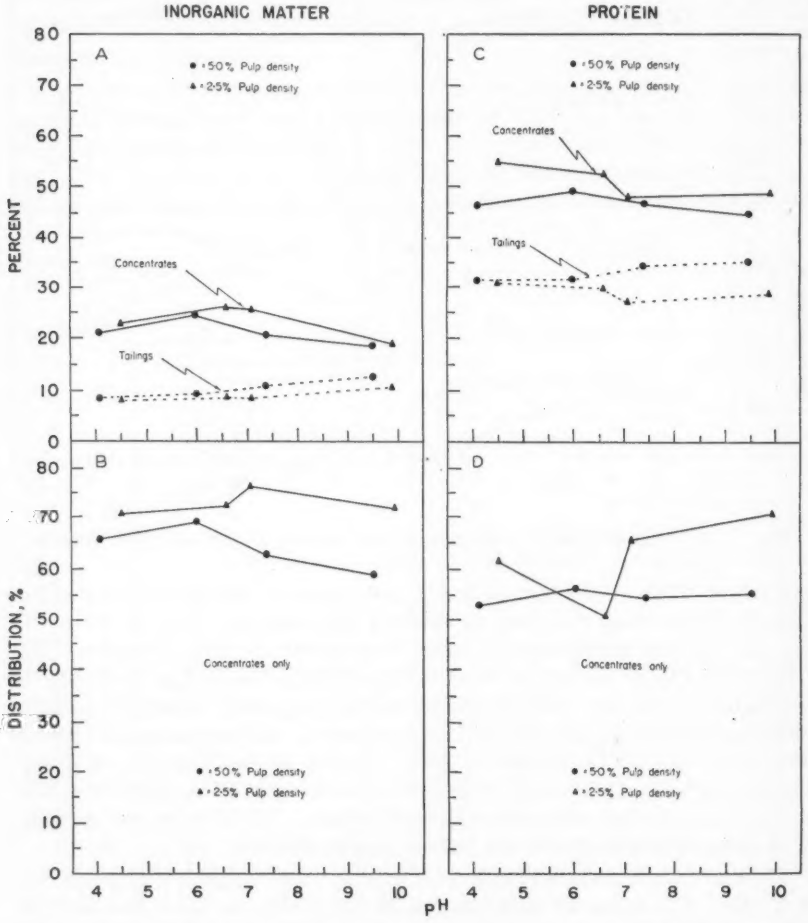

FIG. 5. *Effects of froth flotation at different pH levels on content and distribution of inorganic matter and protein of mustard seed.*

has been substantially enriched in mineral matter, a maximum occurring in the pH range from 6 to 7. The ash content of concentrates and tailings tended to converge at pH values of 9 to 10, this effect being more pronounced at the higher pulp density. From 70 to 75% of the total inorganic matter of the more dilute pulp was distributed to the concentrates over the pH range. Appreciably less inorganic matter was found in the concentrates at the higher pulp density, and the reduction effected by high pH values was accentuated.

Protein Distribution

The protein content of water-extracted mustard screenings was approximately 43%, while feed samples showed values between 40 and 41%. The graphs in Fig. 5, *C*, *D*, describe the per cent of protein and its distribution in the concentrates over a range of pH values. There was substantial concentration in the froth, which was more pronounced at the lower pulp density. While high pH values tended to reduce protein content of the froth the actual amount distributed thereto was not reduced. Minima in the graphs for distribution of protein to the froth fraction are indicated, the lower pulp density being more affected in this respect.

Calculation of protein content on an ash-free basis results in the graphs in Fig. 6. The comparable protein contents of feed at pH 6 were 49 to 50%. The inflections in the graphs indicated for distribution and protein content at the lower pulp density, Fig. 5, *C*, *D*, are greatly accentuated when data

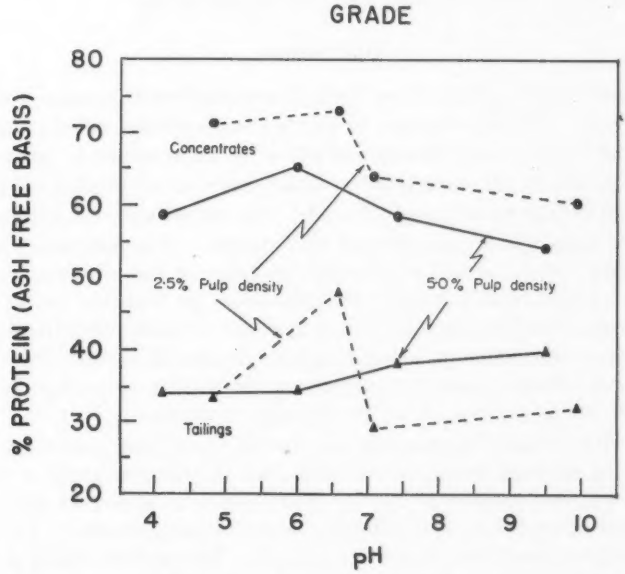

FIG. 6. *Effects of froth flotation at different pH levels on protein content (ash-free basis) of mustard seed.*

are expressed on an ash-free basis It is apparent that the protein contents of concentrates and tailings were greatly affected by both pH and pulp density.

Effects of Flotation on Quality of Oil and Protein

Oils from concentrates tended to be darker and less viscous than oils from tailings. However, the pH at which flotation occurred influenced the extent of these differences and the iodine number of the oil. Oil from mustard pulp floated at pH 6 gave iodine numbers of 125 and 88 for concentrates and tailings, while corresponding values for flotation at pH 7.4 were 115 and 123. The iodine number of oil from feed was 119, a value approximately equal to that from the weighted averages of oils obtained by flotation at the specified pH levels.

Somewhat similar effects were noted for quality of mustard protein from concentrate and tailing fractions as judged by the degree of dispersion. Concentrates obtained in flotation under acid conditions yielded protein that was more readily dispersed than that of the corresponding tailings. However, flotation at pH 7.4 showed a tendency for more of the readily peptized material to occur in the tailings. The method of dispersion (4) specified a peptization period of three hours, which was found inadequate for mustard. Consequently, these results may be considered indicative but not conclusive. They do, however, suggest that some protein fractionation, as well as concentration, occurred concomitantly with oil concentration.

Discussion

These preliminary results show that oil-enriched concentrates result from the application of froth flotation to slurries from pebble-milled seeds. The judicious selection of pulp density and pH of flotation results in up to 90% of the oil occurring in the concentrates, which have an oil percentage approximately double that of the original seed. The distribution of inorganic and nitrogenous materials is also affected by flotation. The differences noted in iodine number of the oil and peptization tendency of the protein also call for comment. These results suggest that flotation, in addition to its use for effecting concentration, may lead to a measure of controlled fractionation. Study of gases other than air would be interesting in this connection. Earlier workers have effected some fractionation of the sodium salts of a mixture of fatty acids, using streams of carbon dioxide or nitrogen (3).

While froth flotation apparently has not been applied previously to the processing of oil from seeds, it has been used in the separation of wool-fat from wool washing effluent (1, 2). It is of interest to note that seed slurries contain their own frothing and collecting reagents, being similar in this respect to other preparations from plant materials (9). The marked effects of protein and inorganic matter on flotation suggest that frothing may relate to the combined effects of oil, inorganic matter, and protein.

This investigation has been limited to a study of the applicability of froth flotation to the production of fractions enriched in oil. Development of methods for the extraction of oil from concentrates has been beyond the scope of the investigation. However, successful integration of pebble-milling and flotation of seed pulps into a feasible oil extraction process depends on removal of oil from the concentrate. Recently described methods for oil extraction (6, 7) involving pebble-milling and centrifuging could, it is believed, be simplified and improved by the inclusion of froth flotation.

Acknowledgments

The authors gratefully acknowledge the helpful advice of J. Klassen throughout the investigation and the assistance of J. Rooke with the analyses.

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THE APPLICATION OF DUST-LAYING OIL TO COTTON[1]

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Abstract

Details of a process for the application of dust-laying oil to cotton fabric are given. The process consists essentially of the mutual coagulation, in the presence of the cotton, of two oppositely charged oil-in-water emulsions. The negative and positive emulsions are stabilized with commercial preparations of sodium ethyl sulphonate methyl-oleamide and cetyldimethylbenzylammonium chloride respectively. The ratio of the two emulsifying agents must be controlled accurately in order to ensure complete coagulation of the oil.

The uniformity of oil distribution on the fabric is satisfactory, and there is little or no tendency for fatty acid or oil to build up on repeated laundering and oiling when carried out in a commercial laundry wash wheel. There is some loss of oil owing to deposition on the wheel, so that it is necessary to allow for 7% oiling in order to obtain 4 to 6% on the fabric.

Introduction

The application of dust-laying oil to hospital bed-clothes for the purpose of reducing dust-borne infection has been the subject of considerable study during the past few years (6, 9, 10, 11). The theoretical and practical aspects of the application of oil to woollen fabrics have already been discussed by Bayley and Weatherburn (3) and by Bayley, Rose, and Weatherburn (2). It is the purpose of the present paper to deal in a similar way with the application of oil to cotton fabrics.

The work is based on the method of Harwood, Powney, and Edwards (6), in which the oiling of cotton fabrics is accomplished by the mutual coagulation, in the presence of the cotton, of two oppositely charged oil-in-water emulsions.

Experimental

Materials Used

A technical white oil, Marcol HX, supplied by Imperial Oil Company, was used in the preparation of the emulsions.

Some preliminary work was carried out using negative emulsions (i.e., emulsions in which the oil drops bear negative charges) stabilized with sodium lauryl sulphate (Duponol WA). It was found however that these emulsions creamed very rapidly and made accurate measurement difficult. Consequently a survey was made of a number of commercially available anionic surface active agents. The stability of emulsions formed with these agents (Table I) was determined in the following manner. The weight of compound indicated in the table was dissolved in 50 ml. of hot, distilled water, 20 gm. oil was stirred in, the volume was made up to 100 ml. with distilled water, and the mixture was passed through a colloid mill. The emulsions were stored in stoppered

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TABLE I

ANIONIC SURFACE ACTIVE AGENTS INVESTIGATED

Reference No.	Name	Type	Manufacturer	Weight used in stability test, gm.
1	Igepon T	$C_{17}H_{33}CONCH_3C_2H_4SO_3Na$	General Dyestuff Corp.	1
2	Igepon AP Extra	Sodium sulphonate of oleic acid ester of aliphatic alcohol	General Dyestuff Corp.	1
3	Igepal C	Polymerized ethylene oxide condensate	General Dyestuff Corp.	1
4	Naccolene F	Modified alkyl aryl sulphonate	National Aniline Division of Allied Chemical and Dye Corporation	1
5	Calsolene Oil HS	Highly sulphonated oil	Imperial Chemical Industries	1
6	Teepol	Sodium secondary alcohol sulphate	Shell Oil Co.	3
7	Aerosol OS	Isopropyl naphthalene sodium sulphonate	American Cyanamid and Chemical Corporation	1
8	Duponol WA	Sodium lauryl sulphate	E. I. du Pont de Nemours Co.	1.5
9	Duponol WA	Sodium lauryl sulphate	E. I. du Pont de Nemours Co.	0.75
10	Nacconol NRSF	Sodium alkyl aryl sulphonate	National Aniline Division of Allied Chemical and Dye Corporation	1
11	Santomerse No. 3	Alkylated aryl sulphonate	Monsanto Chemical Co.	1
12	Aerosol OT	Dioctyl ester of sodium sulphosuccinic acid	American Cyanamid and Chemical Corporation	1

bottles at room temperature for a period of two months. At the end of this time the bottles were shaken thoroughly and allowed to stand undisturbed overnight. The appearance of the emulsions on the following morning is shown in Fig. 1.

Breakdown of the emulsion with the separation of clear oil is apparent in those emulsions stabilized with Igepon AP Extra (No. 2) and with Naccolene F. (No. 4). With these two exceptions the emulsions have been arranged in order of their tendency to cream, i.e., to separate into two layers, the upper one of which contains a high proportion of oil, while the lower one is largely water. This property does not prohibit the use of these emulsions in the oiling process, since the oil is readily redispersed by gentle mixing, but it does tend to make accurate measurement more difficult, and, as will be shown later, accuracy of measurement is of considerable importance in the oiling of cotton by the proposed method.

The majority of the emulsions foamed excessively on milling. This property, while not objectionable in so far as the oiling process is concerned, might present some difficulty in the preparation of emulsions on a large scale. The compounds are divided into three groups according to their tendency to foam on violent agitation.

Group A (*Very little foaming*)

Igepon T
Igepon AP Extra
Igepal C

Group B (*Moderate foaming*)

Naccolene F
Calsolene Oil HS

Group C (*Excessive foaming*)

Teepol
Aerosol OS
Aerosol OT
Duponol WA
Nacconol NRSF
Santomerse No. 3

It is apparent that Igepon T shows the greatest promise from the standpoint of emulsion stability and foaming properties. This compound was therefore selected for further study.

Triton K-60 (cetyldimethylbenzylammonium chloride) was used in the preparation of the positive emulsion.

The cotton sheeting used had a thread count of 76 by 67 threads per inch and a weight of 4.6 oz. per sq. yd. For the laboratory experiments the cotton was freed from water-soluble sizing materials by immersion for one hour in boiling distilled water, followed by a second one hour immersion in boiling water and three rinses in cold water. This desizing treatment was omitted on the cotton used for the pilot plant trial.

Distilled water was used for all of the laboratory work, while for the pilot plant trial Ottawa city water, having a hardness of 4.5 to 5.0 grains calcium carbonate per Imperial gallon, was used.

Preparation of Type A Emulsions

Two stock emulsions, designated "Type *A*," were prepared as follows.

Material	Negative emulsion	Positive emulsion
Oil, gm.	200	200
Igepon T, gm.	20	—
Triton K-60, gm.	—	20
Water (65° C.), ml.	742	742

PLATE I

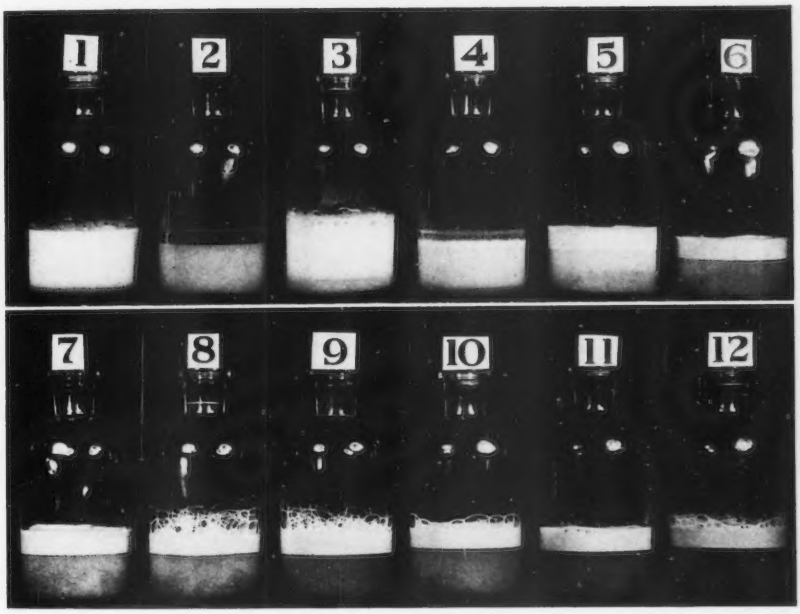

FIG. 1. *Emulsion stability test.*

The emulsifying agent was dissolved in the hot water, the oil was stirred in, and the mixture was passed through a colloid mill. Better emulsions were obtained with Igepon T when the oil was heated to 65° C. before mixing. This was not necessary in the case of the Triton K–60 emulsion. The emulsions were found by analysis to contain 20.0 ± 0.2 gm. oil per 100 ml.

Adsorption of Oil by Cotton

It is well known that cotton, when immersed in water, acquires a negative charge (4, 5, 8). It is to be expected therefore that the adsorption of oil by cotton will be greater from a positively charged emulsion than from one that is negatively charged. This fact was confirmed by carrying out experiments similar to those previously described for the measurement of the adsorption of oil by wool (3). A 10 gm. sample of cotton, cut into small pieces, was agitated in a mixture of 200 ml. of water and 10 ml. of Type *A* negative emulsion at 40° C. Samples of the emulsion were withdrawn for analysis at intervals of 5, 10, 20, and 40 min. The experiment was repeated using 10 ml. of Type *A* positive emulsion. The results are given in Fig. 2.

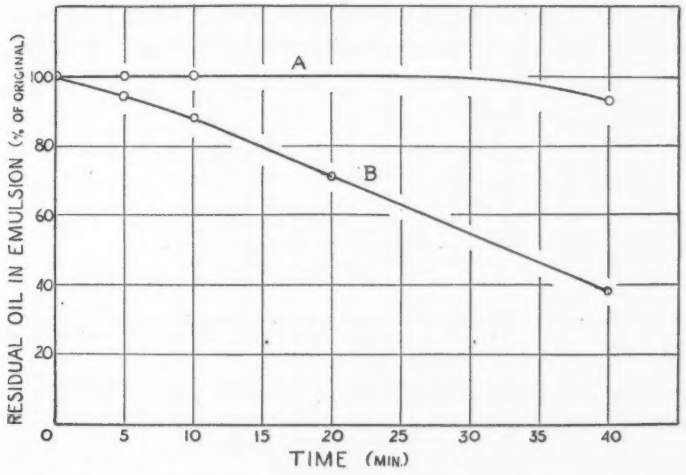

FIG. 2. *Adsorption of oil by cotton. A—Negative emulsion; B—positive emulsion.*

Balance Test

Since the electrical attraction of the cotton for either one of the emulsifying agents is not sufficient to cause complete exhaustion of the treating bath, the deposition of oil on the fabric must be accomplished by the mutual coagulation of two oppositely charged emulsions. It follows that the two emulsifying agents must be present in the proper proportions to bring about complete coagulation of the oil. If either is present in excess, some oil will remain dispersed, and complete exhaustion of the bath is impossible. In order to

determine the optimum ratio of the two emulsifying agents the following "balance" test was devised.

To each of seven test tubes containing 5 ml. of Type *A* positive emulsion was added an amount of negative emulsion varying from 2 to 5 ml. in increments of 0.5 ml. The tubes were stoppered, shaken, and allowed to stand. A marked coagulation was evident in some of the tubes within a few minutes, and after one hour the contents of these tubes had separated into two distinct layers, the lower of which was practically clear water. The contents of the remaining tubes remained milky in appearance. The tubes that showed rapid coagulation were those containing from 3.0 to 4.5 ml. of the negative emulsion, i.e., the optimum ratio of negative to positive emulsifying agent is approximately $\frac{3.75}{5} = 0.75$, and the "usable range" is from about $\frac{3}{5} = 0.6$ to $\frac{4.5}{5} = 0.9$.

In order to check the validity of these conclusions a series of oiling experiments was carried out as described in the preceding section. The 10 gm. sample of cotton was agitated for two minutes in a mixture of 200 ml. of water and 3.5 ml. of Type *A* negative emulsion at 40° C. Then 7 ml. of positive emulsion was added (ratio 0.5) and the stirring continued. Samples of the

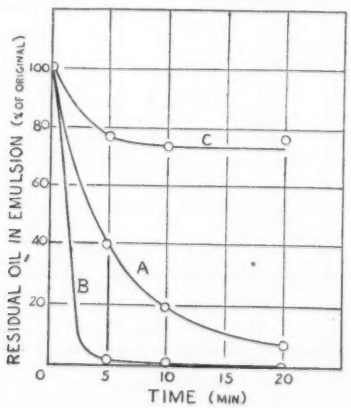

FIG. 3. *Effect of emulsifying agent ratio on oil adsorption by cotton. A—Ratio 0.5 (excess positive); B—ratio 0.75 (optimum); C—ratio 1.0 (excess negative).*

bath were withdrawn for analysis at 5, 10, and 20 min. intervals, the time being measured from the addition of the positive emulsion. The experiment was repeated with negative : positive ratios of 0.75 and 1.0, keeping the total volume of emulsions used constant. The results, calculated as percentages of the total oil used, are given in Fig. 3.

It is apparent that the balance test gives a satisfactory indication of the performance to be expected in the actual oiling operation. The importance

of selecting the correct ratio between the two emulsifying agents is also emphasized.

Order of Addition of Emulsions

Harwood, Powney, and Edwards (6) recommend that the positive emulsion be added first, followed by the negative. In the preliminary work with Duponol WA there was some indication that more rapid exhaustion of the bath is obtained if this order is reversed. This has been confirmed with Type *A* emulsions. The oiling procedure described in the preceding section was repeated using a ratio of 0.75 but reversing the order of addition of the emulsions. The results are given in Fig. 4. In plotting these figures the

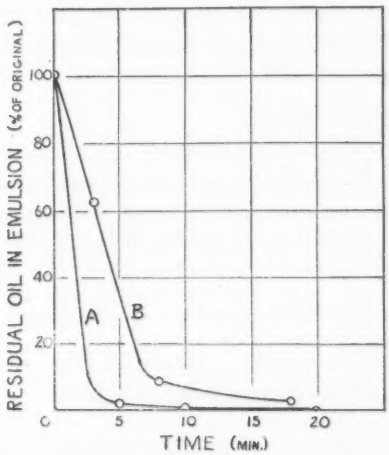

FIG. 4. *Effect of order of addition of emulsions on oil adsorption by cotton. A—Negative emulsion added first; B—positive emulsion added first.*

small amount of oil adsorbed by the cotton from the positive emulsion, prior to the addition of the negative emulsion, has been neglected. The initial point on this curve should obviously be slightly less than 100%.

It is apparent that the deposition of oil is more rapid when the negative emulsion is added first, followed by the positive. This is probably explained by the fact that cotton shows a much stronger selective adsorption for the positive emulsifying agent than for the negative (see Fig. 2). When the positive emulsion is added first, the cationic agent is partially adsorbed by the cotton, with the result that the ratio between the two emulsifying agents is upset, and there is, in effect, an excess of negative emulsifying agent present. When the negative emulsion is added first there is little or no selective adsorption by the cotton, and consequently the ratio between the two emulsifying agents is unchanged.

Influence of pH of the Emulsions

The influence of the pH of the emulsion on the rate of adsorption of oil by cotton was investigated for both negative* and positive emulsions. Within the range studied (pH 3.1 to pH 8.3) it was found that the rate of exhaustion of the oil-bath decreased with increasing pH of the negative emulsion, and increased with increasing pH of the positive emulsion. It has been shown (7) that the magnitude of the negative charge on cellulose increases in alkaline solution and decreases in acid solution. This variation in the magnitude of the charge on the cotton results in varying degrees of attraction for the positive emulsion and of repulsion for the negative emulsion, and undoubtedly accounts for the pH effects noted above.

The pH values of the two emulsions were: negative—6.8; positive—4.0. Adjustment of the pH does not result in any advantage from the standpoint of total oil adsorbed, and hence, in subsequent work, the pH was not adjusted.

Preparation of Type B Emulsions

In the wool oiling process (2) emulsions containing 70% oil and 1.75% Triton K–60 by weight have been found satisfactory. It was found, however, that 70% oil emulsions are not readily formed with Igepon T, and therefore the oil content of the negative emulsion was reduced to 60%. The concentration of Igepon T was reduced to 1.32% so that the two emulsions would contain equivalent amounts of negative and positive emulsifying agents. $\left(\frac{1.32}{1.75} = 0.75, \text{ the optimum ratio}\right)$.

The composition of these emulsions was as follows:

Material	Negative emulsion, % by weight	Positive emulsion, % by weight
Oil	60.00	70.00
Igepon T	1.32	—
Triton K–60	—	1.75
Water	38.68	28.25
	100.00	100.00

The method of preparation was the same as that described for Type *A* emulsions. These emulsions were designated "Type *B*." They differ from Type *A* not only in the increased oil content but also in the ratio of emulsifying

* *This work was carried out using a negative emulsion stabilized with Duponol WA, during the preliminary stages of the research. The conclusions reached should apply equally well to emulsions stabilized with Igepon T.*

agent to oil, which has been reduced from 10% in the Type *A* emulsions to 2.2% in the negative, and 2.5% in the positive Type *B* emulsion.

In order to test further the stability of these emulsions, a series of balance tests was carried out on both Type *A* and Type *B* emulsions at intervals over a period of two months. The Type *B* emulsions were diluted (150 gm. made up to 500 ml. with water) in order to make the oil content approximately the same as that of the Type *A* emulsions. The essential difference between the two pairs of emulsions was therefore in the amount of emulsifying agent. The final composition of the four emulsions (in gm. per 100 ml.) was as follows:

	Type *A*		Type *B*	
	Negative	Positive	Negative	Positive
Oil	20	20	18	21
Emulsifying agent	2	2	0.40	0.53

Typical balance tests are illustrated in Figs. 5 and 6. Each tube shown in Fig. 5 contained 5 ml. of positive, and 2 to 5 ml. of negative Type *A* emulsion, while each tube shown in Fig. 6 contained 5 ml. of positive, and 3 to 6 ml. of negative Type *B* emulsion.

The optimum ratio was calculated as before from the mid-point of the coagulation range, and the "usable range" from the two extremes. There were slight variations in the test from day to day, possibly owing to difficulty in obtaining homogeneous samples, or to small inaccuracies in measurement, but there was no indication of a consistent change in the properties of the emulsions during the two month period. On averaging the results of all of these tests it was found that the optimum ratio was 0.74 for both types of emulsions, but that for the Type *A* emulsions the "usable range" was 0.6 to 0.9, whereas for Type *B* the "usable range" was only 0.72 to 0.76.

It may be concluded that when Type *B* emulsions are used, they must be balanced accurately in order to obtain complete deposition of the oil. When larger amounts of emulsifying agents are used (e.g., Type *A* emulsions) satisfactory oiling can be obtained over a much wider range of concentrations, and consequently more latitude is allowable in the preparation and measurement of the emulsions.

Laboratory Scale Trial of Process

In order to carry out the complete process on a small scale, use was made of a Launderometer (1). Samples of cotton sheeting weighing approximately 10 gm. were laundered and oiled according to the following formula.

Operation	Material	Temperature, °F.	Time, min.
1. Suds	150 ml. built soap solution	160	10
2. Suds	150 ml. built soap solution + bleach	160	10
3. Rinse	150 ml. water	160	3
4. Rinse	150 ml. water	160	3
5. Rinse	150 ml. water	160	3
6. Sour	150 ml. water + 4 ml. 0.75% Na_2SiF_6 solution	120	3
7. Oiling	(*a*) 150 ml. water + 5 ml. negative emulsion	120	2
	(*b*) 5 ml. positive emulsion	120	8

Note:—The built soap solution contained 0.3% neutral soap and 0.1% sodium metasilicate. In the bleaching operation, sodium hypochlorite was added to give a concentration of approximately 0.01% available chlorine.

The pH of the solution at the conclusion of the souring operation was 3.60 to 3.75.

Type B emulsions were diluted so that 5 ml. of negative + 5 ml. of positive contained sufficient oil to give approximately 7% oil on the cotton.

At the conclusion of the oiling operation, the samples of cotton were removed, allowed to drain into the jars, and dried in air. The oil content was determined as described previously (2). The residual bath was poured from the jars and its total oil content was determined. It was observed that some oil had deposited on the sides of the jars. Consequently these were rinsed with isopropyl alcohol, followed by petroleum ether, and the oil content of the rinsings was determined separately. The amounts of oil recovered from the fabric, from the residual bath, and from the sides of the jars are each expressed as a percentage of the total oil used. The oil not accounted for in this way is recorded in the "Loss" column.

The above tests were carried out using (*a*) the complete formula, (*b*) the complete formula with the omission of the bleach, and (*c*) the oiling operation only. From the results obtained (Table II) it may be observed that (*a*)

TABLE II

OIL RECOVERY IN LAUNDEROMETER TRIAL

Treatment	Oil recovered, % of oil used				Oil on fabric, % by weight
	On fabric	In residual bath	On launderometer jar	Loss	
Complete formula	77.3	3.2	6.3	13.2	4.9
	81.5	2.8	6.0	9.7	4.9
Complete formula omitting bleach	81.5	2.5	4.8	11.2	5.3
	84.8	3.0	6.4	5.8	5.2
	78.6	2.4	4.8	14.2	5.2
Oiling only	78.7	5.1	8.9	7.3	4.9
	77.1	2.9	5.5	14.5	4.9

PLATE II

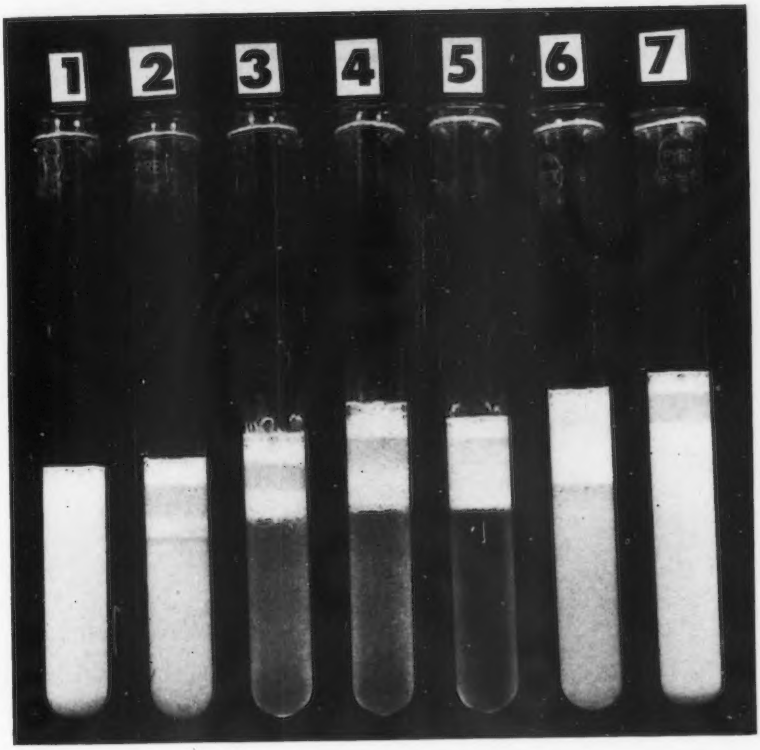

FIG. 5. *Balance test. Type A emulsions.*

PLATE III

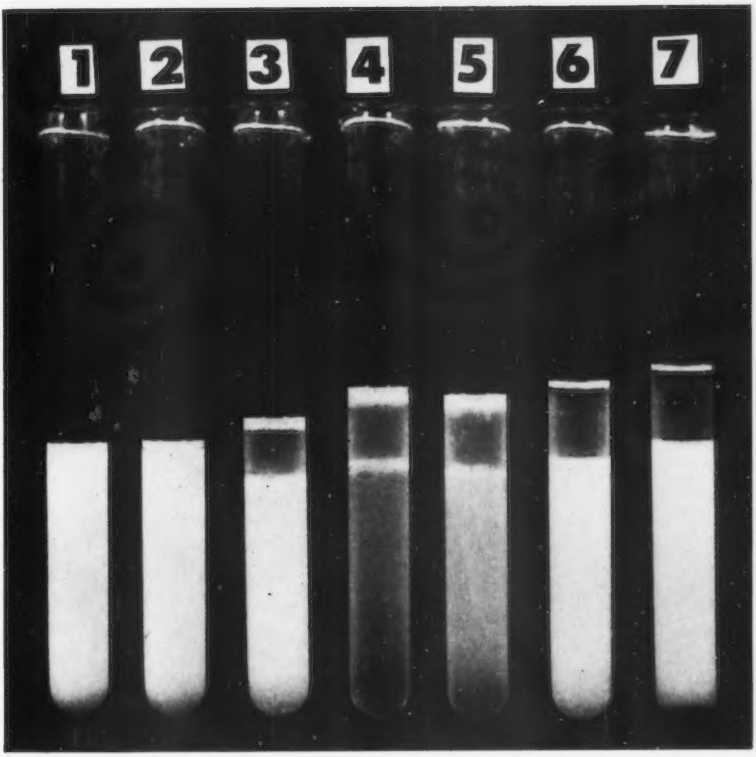

FIG. 6. *Balance test. Type B emulsions.*

approximately 80% of the oil used is retained by the fabric, (*b*) the preliminary laundering, with or without the use of bleach, has no effect on the oiling process, and (*c*) from 4 to 9% of the oil used is deposited on the sides of the containing vessel.

Pilot Plant Trial of Process

For the purpose of carrying out a trial on a larger scale, a 24 by 24 in. monel metal commercial laundry wash wheel was used. The 15 lb. load of cotton sheeting was laundered and oiled according to the following formula.

Operation	Material	Water level, in.	Temperature, °F.	Time, min.
1. Suds	Built soap solution	3	160	10
2. Suds	Built soap solution	3	160	10
3. Rinse	Water	7	160	3
4. Rinse	Water	7	160	3
5. Rinse	Water	7	160	3
6. Sour	Sodium silicofluoride	7	120	10
7. Oiling	(*a*) Negative emulsion	7	120	2
	(*b*) Positive emulsion	7	120	8

Note:—The built soap solution contained 10% neutral soap and 3.3% sodium metasilicate. Approximately 1.5 litres was required for each suds.

The sour was added in the dry form, approximately 50 gm. per load being required to reduce the pH to 4.5–5.0. The souring time could have been reduced to three to five minutes by adding the sour as a 1% aqueous solution.

Type B emulsions were diluted so that 1 litre of each was required to give 7% oil on the load.

After oiling, a sample of the residual bath was removed for analysis. It was observed that there was some oil on the surface of the bath liquor, and also that the interior of the wash wheel was coated with a film of oil. The load was removed, hydro-extracted, and dried. Samples of the cotton were removed for oil and fatty acid analysis immediately after the souring operation and again after the oiling operation. The results of these analyses are given in Table III. The weight of oil deposited on the cotton in each oiling operation, expressed as a percentage of the weight of oil used, is also given.

The analyses of the residual bath liquors are misleading, owing to the fact that oil collected at the surface of the liquor in the wash wheel, and, on sampling, a high proportion of this oil was obtained. In the analysis of the residual baths from the first two loads, the samples were shaken vigorously to disperse the oil before removing aliquots for analysis. The sample from the third load was poured into a separatory funnel and allowed to stand for 10 min. before portions were drawn off for analysis. The figures obtained (Table III) are of no value as a criterion of the degree of exhaustion of the treating bath, but they do indicate that the coagulation of the emulsions has been virtually complete, and also that a certain percentage of the precipitated oil has not been picked up by the cotton.

TABLE III

ANALYSIS OF COTTON FOR FATTY ACID AND OIL CONTENT

Number of oilings	Samples removed prior to oiling		Samples removed after oiling		Oil deposition on cotton (% of oil used)	Oil content of residual bath (% of oil used)
	Fatty acid, %	Oil, %	Fatty acid, %	Oil, %		
1	0.36		0.32	3.0		34.8
	0.27		0.46	5.0		28.2
	0.30		0.33	3.3		
			0.35	3.7		
			0.40	5.3		
			0.37	3.8		
	0.31		0.37	4.0	57.3	31.5
2	0.18	0.7	0.26	4.7		23.3
	0.38	0.7	0.28	5.5		17.6
	0.23	1.0	0.30	5.1		
	0.25	0.8	0.33	5.2		
	0.22	0.9	0.27	5.5		
	0.30	1.1	0.25	4.6		
	0.26	0.9	0.28	5.1	60.0	20.4
3	0.25	1.0	0.37	6.2		0.8
	0.29	1.4	0.35	5.3		1.3
	0.30	1.4	0.29	6.0		
	0.23	1.5	0.32	5.7		
	0.25	0.8	0.29	6.7		
	0.23	0.9	0.26	5.0		
	0.26	1.2	0.31	5.8	65.7	1.1

Discussion

In general the process appears to be satisfactory. There is no build-up of fatty acid on repeated oiling, and the build-up of oil is slight, since the residual oil content of the cotton is reduced to approximately 1% after laundering. The uniformity of oil distribution is quite satisfactory. There is, however, considerable loss of oil owing to deposition on the interior of the wash wheel, so that it is necessary to allow sufficient emulsion for 7% oiling in order to obtain 4 to 6% on the fabric. This film of oil was readily removed from the wash wheel by giving it one suds with soap and alkali followed by one or two rinses with water.

Satisfactory oiling has been accomplished with Type *B* emulsions. The positive emulsion is identical with that recommended for the oiling of wool (2), and the use of these emulsions would therefore be desirable in plants engaged in the oiling of both wool and cotton. On the other hand, these emulsions must be prepared and measured with considerable accuracy. The feasibility of doing this on a large scale can be determined only by actual plant trial. Increasing the proportion of emulsifying agent in both emulsions allows more latitude in handling, and this advantage must be balanced against the increased cost of materials.

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THE THERMAL INSULATION OF A DOUBLE PILE FABRIC AND ITS VARIATION WITH THICKNESS[1]

P. LAROSE[2]

Abstract

Results of the measurement of the thermal insulation of a double pile fabric, the thickness of which was varied by compression, are given. Within the limits of the experiments the thermal insulation was found to vary linearly with thickness. The slope of the line corresponds to a value of 4.6 clo per in. thickness. The results are discussed in regard to those obtained by other investigators.

Introduction

The thermal insulation of fibrous materials, either in the loose state or as knitted or woven fabrics, has been measured by a number of investigators. In some cases attempts were made to derive a relation between thermal insulation and density by varying the density of the material (Finck (2)). In other tests the thickness of the material was varied while keeping the density constant (Babbitt (1)). Some of the investigators by using different materials varied thickness and density at the same time (Sale and Hedrick (6)) (Speakman and Chamberlain (7)). The present paper gives results of tests carried out on a fabric, the thickness of which was varied by compression. This procedure eliminates complicating factors arising from differences in construction when comparing different materials or fabrics. It also gives directly a relation between density and thickness, since the weight of material remains the same. Moreover, it has the advantage of giving directly the effect to be expected from the compression of such a fabric during wear.

The material tested was a double pile fabric of $\frac{5}{8}$ in. nominal thickness, such as that used for lining flying clothing worn by some of our aircrew during the war. The pile was made of 2/18's worsted yarn with 64's quality wool, and was woven on to a cotton ground fabric made with 2/20's yarn of warp and 1/8's in the weft. The number of ground ends per inch was 60, pile ends 20, picks per inch 48. The construction was such that the tufts were continuous from one side of the fabric to the other, in other words, the same tuft projected on both sides, so that the number of tufts per square inch, namely 160, was necessarily the same on either side. The total weight of the material was 23 oz. per sq. yd., of which 14 oz. was wool pile and 9 oz. ground fabric. The compressibility of this fabric as measured by the reduction of thickness when the pressure is increased from 0.1 lb. per sq. in. to 1.0 lb. per sq. in. was about 50%. The pressures required to compress the fabric to the thicknesses determined during the experiment were estimated from the known compressi-

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bility curve for this fabric. The pressures read from the curve are given in Table I. The range covered includes all the pressures to which such a fabric might be subjected in the course of normal wear. Kitching (unpublished work) has measured the pressures under an airman's clothing while the latter was in a sitting position and found them to be less than 1.0 lb. per sq. in. in most regions, although this figure was exceeded in some instances but was never more than 2.0 lb. per sq. in. For a man who is walking about and whose clothing is not being pressed against any object, the pressure is bound to be quite small.

Tests were also carried out on a similar fabric but made with a coarser wool (60's quality) in the pile, for the purpose of determining the effect of temperature. Since the tests were made for three different thicknesses of the material, the results, as well as those obtained with two samples of felt tested in the same way, are included for comparison.

Method

The thermal insulation of the fabric was determined with the apparatus described by Niven (5) for the measurement of fibreboard insulation. It is a typical hot plate apparatus used extensively to measure the thermal conductivity of homogeneous building materials. It is very similar to an earlier apparatus described by van Dusen (8). The hot plate is sandwiched between two samples of the material to be tested, which in turn are confined by two cold plates. Lateral heat flow is prevented by means of a guard ring. The hot plate and the cold plates are suspended from rails on which they are free to move. An arrangement is also provided by which the plates can be pressed against each other so as to compress the samples contained between them. The samples tested measured 18 by 18 in. including the area over the guard plate. In all the tests the cold plates were maintained at 33° F., and the temperature of the hot plate was adjusted to give a temperature difference of 26° to 30° F. except where otherwise indicated. The thickness of the sample was determined by measuring with a micrometer caliper the distance separating the plates at the four corners and taking the mean of the four readings. Before readings of temperature and heat input were taken, the apparatus was allowed to stand until equilibrium conditions were attained. Half a day was usually sufficient but in many cases the sample was allowed to stand overnight and readings were taken the next day. In order to average the effect of slight fluctuations, readings were taken every 15 min. for a period of two hours or more.

Results

The results of our experiments are summarized in Tables I, II, and III. Thickness was determined as described under "Method." The compression pressure was obtained from the compressibility curve, as mentioned in the introduction. The bulk density is readily calculated from the weight of the material per unit area and the thickness. The conductance is calculated

from the known conditions of the experiments, while the insulation is obtained from the conductance by conversion of units.

Δt in Table II represents the difference of temperature between the hot plate and the cold plates.

TABLE I

THERMAL INSULATION OF PILE FABRIC FOR VARIOUS DEGREES OF COMPRESSION. PILE MADE FROM 64'S WOOL

Thickness, in.	Compression pressure, lb./in.^{2}	Bulk density, lb./ft.^{3}	Conductance, B.T.U./ft.^{2}/hr./° F.	Insulation	
				Clo	Clo/in. thickness
0.585	0.0	3.28	0.43_0	2.64	4.52
0.459	0.05	4.19	0.54_2	2.10	4.57
0.408	0.12	4.70	0.60_6	1.87	4.59
0.345	0.23	5.56	0.70_8	1.61	4.65
0.305	0.35	6.29	0.79_8	1.42	4.67
0.262	0.57	7.33	0.93_8	1.21	4.63
0.220	0.90	8.72	1.13_0	1.00	4.57
0.171	2.0	11.2	1.55_2	0.73	4.28

TABLE II

THERMAL INSULATION OF PILE FABRIC FOR VARIOUS DEGREES OF COMPRESSION AND FOR VARIOUS MEAN TEMPERATURES. PILE MADE FROM 60'S WOOL

Thickness, in.	Bulk density, lb./ft.^{3}	Conductance, B.T.U./ft.^{2}/hr./° F.	Insulation, clo	Δt, °F.
0.537	3.53	0.48_7	2.33	36.0
0.428	4.42	0.60_4	1.88	38.5
0.428	4.42	0.59_9	1.90	45.4
0.428	4.42	0.59_8	1.90	52.3
0.428	4.42	0.59_7	1.91	59.1
0.428	4.42	0.60_4	1.88	93.4
0.193	9.80	1.35	0.84	47.1

TABLE III

THERMAL INSULATION OF TWO SAMPLES OF FELT

Thickness, in.	Bulk density, lb./ft.^{3}	Conductance, B.T.U./ft.^{2}/hr./° F.	Insulation, clo	Δt, °F.
0.147*	10.4	1.79	0.63	—
0.123*	12.4	2.05	0.56	—
0.451**	9.15	0.60	1.90	44.8

** White and high quality felt from fine wool.*

*** Coarse punched felt on hessian base and with coarse hair.*

Since we are dealing with clothing material we have chosen to express the insulation in 'clo' units. The clo unit has been defined as "the amount of insulation necessary to maintain in comfort a sitting–resting subject in a normally ventilated room (air movement 20 ft./min. or 10 cm./sec.) at a temperature of 70° F. (21° C.) and a humidity of the air which is less than 50 per cent." (3).

The clo unit is equal to $0.18 \frac{°C.}{Cal./hr./sq.\ m.}$

or $0.88 \frac{°F.}{B.T.U./hr./sq.\ ft.}$

The above results for thermal insulation have been plotted against thickness in Fig. 1.

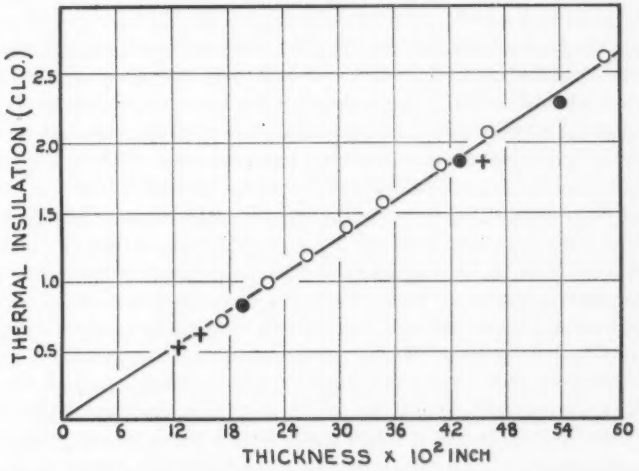

FIG. 1. *Curve showing the relation between the thermal insulation of pile fabrics and thickness.*

Discussion

Previous work carried out with fibrous materials has indicated that, within certain limits at least, the insulation varies linearly with thickness, but the relation was more or less obscured by complicating factors introduced by the use of materials that differed in some way or other when the thickness was varied. The work of Babbitt on fibreboard is an exception (1). He varied the thickness by removing material by abrasion, and not by compression, so that the density of the board was practically constant in all his experiments. His results for rock wool also apply to material with constant density. Nevertheless, his results are not comparable with those to be expected with a fabric under various degrees of compression. It is worthy of note that the insulation value per inch thickness was higher for the materials of lower density, e.g., the fibreboard of 12.2 lb. per cu. ft. gave an insulation (per inch thickness)

of 3.15 clo as against 2.65 clo for the board of 17.8 lb. per cu. ft. The rock wool gave a much better insulation, 4.25 clo for density of 7.9 lb. per cu. ft. and 4.83 clo for 7.1 density, but these two results are not strictly comparable, since the rock wool was not in the same form in the two experiments. Except for a surface effect in the fibreboard, Babbitt's results when plotted against thickness give practically a straight line passing through the origin. This shows that insulation was proportional to thickness within the limits of his experiments.

Marsh (4) obtained his results by testing materials that differed widely not only in thickness but also in density. He concluded that there was no relation between insulation value and density, but that there was a rough linear relation between insulation value and thickness. However, his curve did not pass through the origin. This he attributed to convection effects. His points are scattered widely about the curve, particularly for materials of low thickness. It should be noted that Marsh used a method in which the sample tested was wrapped around a cylinder and had therefore one of its faces exposed to the ambient air. Moreover, the thickness was taken as that under a certain arbitrary pressure. As his results are not expressed in terms that permit the calculation of the absolute conductivity of his materials, it is impossible to derive any relation from them.

The results given by Sale and Hedrick (6) were, like those of Marsh, obtained with widely different materials varying in thickness and density, and under such conditions that the materials were not completely enclosed, but had one surface exposed to the air. Nevertheless, a much better curve was obtained when their results were plotted. They did not show such a pronounced scatter as Marsh's results. Their curve also gave a zero intercept, which was explained by a surface effect. The best curve through Sale and Hedrick's results gives a slope of 2.93 clo per in., but, if the points for thicknesses less than 0.16 in. are omitted, a fairly satisfactory curve passing through the origin can be drawn. This curve has a slope of 3.91 clo per in.

Finck (2) measured the insulation of various materials at constant thickness but varied the density of packing. All his curves giving the relation between the insulation and density show a maximum (minimum when the points are plotted as conductance against density) for a particular density, which, for most materials, was around 5.0 lb. per cu. ft., kapok forming an exception with its maximum insulation at a density of about 1.0 lb. per cu. ft.

Speakman and Chamberlain (7) also found with some of the materials they investigated a decided change in the insulation as the density was varied. At the low densities their curves exhibit a maximum insulation (minimum conductivity) or a plateau for a narrow range of densities, but as the density is increased above a certain value ($\backsim$ 10 lb. per cu. ft.) the insulation decreases at first slowly, then more rapidly.

Fig. 1, in which are plotted our results, shows distinctly that a straight line relation was obtained for the insulation in respect to thickness for all densities in the range of 3.2 lb. to 11.2 lb. per cu. ft. A close examination of the

insulation values per inch thickness in Table I reveals, however, a tendency for the insulation to increase and then decrease, with a maximum at a density of about 6 lb. per cu. ft., but, in view of the slight differences noted and the possible experimental error, the straight line was considered to represent the trend with sufficient accuracy.

It should be pointed out that in spite of the range of densities covered in our experiments, a range representing that which might be met in practice with such fabrics, the variation in this respect was not as large as that observed in the experiments of van Dusen or of Finck. Our results for the insulation of the double pile fabric at the lowest density and at a density of 8.7 lb. per cu. ft. differ by only 3.3 and 2.2%, respectively, from the highest value obtained at a density of 6.3 lb. per cu. ft. These differences are considered to be of the same order as the experimental error. The result for the highest density of 11.2 lb. per cu. ft. is the only one that shows a difference, $8\frac{1}{2}$%, that may be significant. Finck's published results do not include wool but his results for the insulation of curled hair show a difference of 8% when the density was varied from 3.6 to 4.6 lb. per cu. ft. In the case of jute, a difference of 15% was obtained in changing the density from 3.5 to 12.3 lb. per cu. ft. Van Dusen got a difference of 19% when the density of wool was varied from 2.5 to 6.3 lb. per cu. ft. These variations are appreciably larger than those obtained in our experiments. Speakman and Chamberlain on the other hand give results that are comparable with ours. A 56's Australian crossbred wool showed a difference of 6.3% in insulation value as its density was changed from 0.8 to 11.0 lb. per cu. ft., but an 80's Australian merino wool showed hardly any variation in insulation as the density ranged between 1.5 and 10.1 lb. per cu. ft. while a 64's merino wool gave a difference of insulation of 2.9% within the same range of densities. It would seem therefore that for low densities, say up to 10 lb. per cu. ft., the insulation value of loose wool changes very little with density and is a function of thickness only.

Examination of Fig. 1 shows that the line drawn through the points representing the results for Table I passes through the origin. This is in agreement with the results of Babbitt already quoted and those of Sale and Hedrick, with the limitations cited above. The results of Speakman and Chamberlain also give straight lines, the slopes of which depend on the densities of the fabrics. The slope of our curve gives an insulation value of 4.60 clo per in., while the results of Table II give a mean insulation of about 4.4 clo per inch. For the purpose of comparison, some of the values obtained by the investigators referred to above are summarized in Table IV.

The above figures indicate that our results correspond more closely to those for loose materials than to the results for fabrics, which are definitely lower. The lower results for fabrics may be attributed to the higher density of the material. The density effect is intensified by the fact that the fibres are not uniformly distributed, and the actual density in the yarn is much higher than the bulk density calculated from the weight of the material and the apparent volume of the fabric.

TABLE IV

THERMAL INSULATION FOUND BY VARIOUS INVESTIGATORS FOR CERTAIN FIBROUS MATERIALS

Investigator	Material	Density, lb./cu. ft.	Insulation, clo/in. thickness
Finck	Kapok	1.0	4.75
Finck	Jute	3.5	4.56
Finck	Sphagnum moss	5.4	4.80
Van Dusen	Wool	6.6	4.65
Babbitt	Rock wool	7.1	4.83
Babbitt	Rock wool	7.9	4.25
Sale and Hedrick	Wool blankets	3.9 – 7.8	3.77
Speakman and Chamberlain	Wool fabrics	15.5 – 26	3.70 – 3.98
Speakman and Chamberlain	Loose wool (64's)	1.5	5.0
Speakman and Chamberlain	Loose wool (64's)	11.0	4.8
Speakman and Chamberlain	Milled fabrics	17 – 18	4.15

A straight line passing through the origin such as we obtained indicates that, even at the lowest density employed, the air is sufficiently broken up by the fibrous mass to render convection effects negligible. At the lowest density reached in our experiments, the fibres are separated by a mean distance of $\frac{1}{8}$ mm., a distance much too small for convection effects to have any importance. By comparing the thermal transmission of kapok layers placed firstly in a vertical position, then in a horizontal position, Finck showed that convection plays a negligible part in heat transmission along a fibrous mass. He concluded therefrom that radiation must be responsible for the changes noted at low densities. On the other hand, at high densities the radiation loss becomes quite small and conduction along the fibres must play a role in accounting for the increase in heat transmission.

Where a straight line relation holds, as in our experiment, it follows from the previous remarks that any increase in heat transfer due to conduction by the fibres must be accompanied by a corresponding decrease in radiation. Increased conduction along the fibres will take place as the density of the mass increases, for the proportion of the space occupied by the fibres increases. At the same time, transfer of heat by radiation must decrease since the path from hot to cold plates becomes more and more broken up by intervening fibres. This follows from the well known principle that intervening walls between radiator and receptor will reduce the amount of radiation owing to the fact that radiation then occurs between bodies with smaller temperature differences. This applies when the temperatures of the intervening surfaces are intermediate between those of the radiator and receptor, conditions that hold in the present instance. However, the increase in conduction through the fibres with increase in density is the result of several effects. In the first place, the increase of fibre substance by itself will increase conduction, as already mentioned, owing to the fact that the heat conductivity of the fibre

is greater than that of air. Secondly, the increase in density will no doubt result in a better contact between fibres and between the fibrous mass and the hot and cold walls. Both these effects have been mentioned by Finck in discussing the results of his experiments. There is a third factor, however, in connection with conduction by the fibres which does not seem to have been considered by previous investigators, namely, the length of the fibres in relation to the thickness of the insulating layer. Finck showed that the direction of the fibres had quite an effect on the value of the insulation, the insulation when the fibres lay perpendicular to the direction of heat flow being in some cases more than double that obtained when they were parallel to the direction of flow. This effect is an important one because it means that for any one type of fibre and given density, a wide range of values, depending on the orientation of the fibres, can be obtained for the insulation. Finck correctly interpreted the effect but failed to mention the fact that this effect could be influenced considerably by the length of the fibres. The short circuiting of the plates by the fibres when these are parallel to the direction of heat flow can occur only if the fibres are longer than the distance separating the plates, otherwise there must be a break in the conduction along the fibres, and heat transfer has to take place through the contact points between fibres. Naturally, the shorter the fibres, the greater the number of such breaks and the greater the resistance to heat flow along the fibres. This effect has probably been disregarded because, in most experiments, the thickness of the layer tested was small or of the same order of magnitude as the length of the fibre. In the case of wool certainly this must be so. Our pile fabric was so constructed that the fibres in the wool tufts constituting the pile were continuous from one side to the other, and in all tests short circuited the hot and cold plates of the apparatus. However, the pile is so cut that the fibres are not all of the same length. At low densities therefore, when there is little pressure applied to the fabric, the contact with the plates would be a poor one, but, as the pressure is increased, not only do more and more fibres make contact with the plates but the contact also becomes closer in that the fibres are more firmly pressed against the plates. It must be pointed out, however, that the pile as a whole does not lie parallel to the direction of heat flow, but makes a small angle with it. Moreover, the wool fibres are not straight but are crimped. Parts of the fibres will therefore lie in various directions quite different from the general direction of the pile.

As the pile is compressed the fibres will be distorted, or they will be bent over. In any case the compression will cause the direction of the fibres to become more and more nearly perpendicular to the direction of heat flow, and this will tend to reduce the transfer of heat by radiation, as was pointed out by Finck. On the other hand, the better contact with the plates that results tends to increase conduction, although the actual path along the fibres does not necessarily become shorter. It would appear from our results that these two opposing effects just about balanced each other.

Acknowledgment

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THE PREPARATION OF HEXACHLOROETHANE IN THE LIQUID PHASE BY CHLORINATION OF TETRA— AND PENTACHLOROETHANE[1]

By Jesse A. Pearce[2]

Abstract

Preliminary investigations showed a slow rate of production of hexachloroethane from chlorine-saturated liquid tetrachloroethane. The addition of some materials that often accelerate similar reactions was not effective here. However, rapid production was obtained by chlorinating tetrachloroethane in the presence of ultra-violet light. The effective wave-lengths appeared to lie between 3150 Å and 3540 Å, and the temperature coefficient between 75° and 100° C. was 1.10. The result indicated that production of hexachloroethane from chlorine-saturated liquid tetrachloroethane was feasible. For the same conditions of illumination and temperature hexachloroethane was produced from chlorine-saturated pentachloroethane at a rate two and one-half times as fast as that in chlorine-saturated tetrachloroethane.

Introduction

In the past the commercial preparation of hexachloroethane has involved preparation of trichloroethylene from tetrachloroethane, followed by chlorination to pentachloroethane, the decomposition of pentachloroethane into tetrachloroethylene, and chlorination of this last product to hexachloroethane.

Two other methods of preparing this product from tetrachloroethane are also known. One method, which depends on the chlorination of tetrachloroethane using ultra-violet light or other light source rich in active rays, probably yields a mixture of penta- and hexachloroethanes (7, 8). Whether this was done using liquid tetrachloroethane or the vapour is uncertain. The other method, involving chlorination of liquid tetrachloroethane in the presence of vegetable charcoal, animal charcoal, bleaching powder, ferric chloride, or aluminium chloride as catalysts, is reported to yield only hexachloroethane (3). The study reported in the present paper was made in 1940, when a large increase in Canadian production of hexachloroethane seemed necessary, and it was suggested by Dr. O. Maass that the possibility of manufacturing this material by direct chlorination of tetrachloroethane in the liquid phase should be investigated.

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Contribution from the Department of Chemistry, McGill University, Montreal, P.Q. Material selected from a thesis presented to the Faculty of Graduate Studies and Research, McGill University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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Thermal Studies

Materials

Initially an attempt was made to use crude tetrachloroethane as currently prepared on a commercial scale. However, this material was unsatisfactory and several methods of purification were attempted. The materials used are described in Table I.

TABLE I

EFFECT OF STARTING MATERIAL ON THE RATE OF FORMATION OF HEXACHLOROETHANE FROM TETRA- AND PENTACHLOROETHANE AT 100° C.

(Illumination variable)

No.	Starting material	Degrees of freedom	Average rate*	Standard deviation
I	Crude tetrachloroethane	—	Decomposition	—
II	Fraction of No. I boiling at 144 to 148° C.	2	3.8	0.36
III	No. II after drying over calcium chloride	4	2.2	0.71
IV	No. III partially chlorinated, then fractionated. Fraction boiling at 145 to 147° C. used.	1	6.4 (2.3, 10.6)	—
V	Tetrachloroethane; b.p., 146.3° C.	5	2.8	2.1
VI	No. V after being subjected to some decomposition by heating with aluminium chloride, followed by fractionation. Fraction boiling at 144 to 148° C. used.	3	2.6	0.77
VII	Mixture; III : V = 2 : 1	7	1.5	0.77
VIII	Pentachloroethane; b.p., 161.7° C.	1	3.2 (1.3, 5.0)	—

* *Rates given in Tables I and III record the percentage of hexachloroethane formed in the reacting mixture per hour, averaged over chlorination periods of about 20 to 36 hr. Those given in Table IV are for chlorination periods of one to four hours.*

Analytical Methods

An analytical method that proved satisfactory was based on the change in boiling point as the quantity of the hexachloroethane in solution was increased. Boiling point calibration curves for hexa- in tetrachloroethane and hexa- in pentachloroethane were established (Fig. 1). Several samples of partially chlorinated tetrachloroethane, when fractionated in a Whitmore column, gave yields of hexachloroethane that did not differ significantly from the amount predicted by boiling point determinations. Pentachloroethane, if present, was not detectable by these fractionations; this supported a previous similar observation (3).

Apparatus

The rate of production of hexachloroethane was readily followed by the boiling point technique in apparatus of the type shown in Fig. 2. Unless otherwise noted these were constructed of Pyrex. The portion designated *A* in Fig. 2 had a capacity of about 50 ml., while the enlarged part, *B*, helped

eliminate bumping of the material into the condenser, *C*, when the material was boiling. The chlorine inlet is shown at *D* and was connected directly to a chlorine cylinder by rubber tubing. Chlorine flow during a boiling point

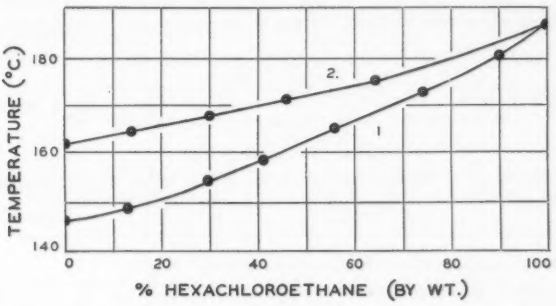

FIG. 1. *Boiling-point–composition curves for solutions of hexa- in tetrachloroethane (Curve 1) and of hexa- in pentachloroethane (Curve 2.)*

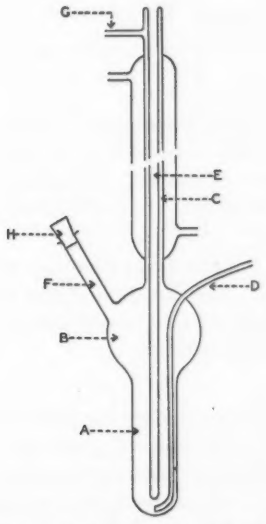

FIG. 2. *General design of chlorination apparatus.*

determination reduced the temperature and was, therefore, stopped with a screw-clamp. At the same time, this made *D* an enclosed space, which helped prevent superheating. In the diagram, *E* designates a thermometer well, which contained a clear, high-boiling oil. Tetrachloroethane and catalyst were introduced through the arm, *F*, which also facilitated cleaning. Excess chlorine was conducted away at *G*. Modifications of this apparatus are described in Table II.

Temperatures of the reaction mixtures were controlled by suitable oil- or water-baths, or direct flame. Boiling-point–composition curves and certain other boiling point determinations were made in an apparatus of similar design, but the portion *A* had a capacity of only 10 ml. and the other dimensions were correspondingly reduced.

TABLE II

EFFECT OF SOME FACTORS ON THE RATE OF FORMATION OF HEXACHLOROETHANE FROM TETRACHLOROETHANE AT 100° C.

(Illumination variable)

Factor	Average rate
Surface area: reaction chamber packed with Pyrex chips	2.2
Surface quality: reaction chamber made from quartz	2.7
Liquid depth: reaction chamber made 7 ft. in length	2.9
Condenser volume: bulb above liquid chamber made 7 ft. in length, i.e., reaction in gas phase above liquid.	2.9
Pressure: reaction at 1¼ atm.	0.4

Chlorination Procedure

A weighed quantity of tetrachloroethane (usually 50 gm.) was introduced into the reaction chamber and saturated with chlorine, while being brought to the desired temperature. Constant introduction of chlorine during the reaction maintained the chlorine content of the mixture as nearly as possible at saturation.

Unless otherwise noted the reaction chambers were subjected to no other pressure than atmospheric. The duration of any reaction varied from 20 to 36 hr., the actual time depending on the conditions of the experiment and the rate of production of hexachloroethane.

Results

It was observed (Table I) that neither the purity of the material nor method of purification had any effect in improving the rate of hexachloroethane production provided the tetrachloroethane had received sufficient purification to prevent its decomposition. Attempts to purify the material by allowing it to stand over potassium hydroxide, followed by distillation, were unsatisfactory, since sufficient alkali was dissolved to cause decomposition during the distillation (9). The data in Table I also indicate that the rate of production from pentachloroethane was not appreciably different from the rate of production from tetrachloroethane.

Examination of the rates of production in different pieces of apparatus indicated that somewhat faster rates occurred in one reaction vessel. These faster reaction rates were attributed to several possible factors, e.g., increased surface to volume ratio of liquid in this chamber. These factors and their

effects on production rates were examined and the results are shown in Table II. Increase in pressure, the only factor having a significant effect on rate, appeared to retard the production of hexachloroethane.

The addition of substances ordinarily believed of value in accelerating chlorinations had no effect on the rate of this reaction (Table III). Many added substances caused charring in the reacting mixture, indicating decomposition of the tetrachloroethane; charring was generally accompanied by a

TABLE III

EFFECT OF ADDED SUBSTANCES ON THE RATE OF FORMATION OF HEXACHLOROETHANE FROM TETRACHLOROETHANE AT 100° C. AND AT THE BOILING POINT OF THE REACTING MIXTURE

(Illumination variable)

Added substance		Average rate	
		At 100° C.	At B.p.
Activated charcoal		Decomposition	—
Aluminium chloride	10.0%	—	Decomposition
	0.5%	—	2.2 (sl. dec.)
	0.2%	3.6 (sl. dec.)	2.7 (sl. dec.)
Ferric chloride	0.2 to 10%	Decomposition	Decomposition
Stannous chloride	2.0%	—	0.6 (sl. dec.)
	0.2%	—	1.2
Nickelous chloride	2.0%	—	0.5
Sulphur monochloride	20%	—	1.1
	2%	—	1.2
	0.2%	—	0.4
Sulphuryl chloride		3.1	—
Benzoyl peroxide		2.9	—
Saturation with water		2.9	—
Nickel gauze		3.2	—

decrease in boiling point. Since dechlorination of the tetrachloroethane vapour is known to occur over charcoal at 400° C. (11), it was suspected that charcoal caused decomposition in the liquid phase at 100° C. Nickel gauze was added to ascertain whether serious corrosion occurred, or whether the reaction rate might be affected, i.e., whether nickel could be used as a reaction vessel. There was practically no corrosion and no change in rate.

It is also evident from Table III that production at 100° C. was preferable to production at the boiling point, while at 25° C. no reaction occurred.

Photochlorination Studies

Since none of the factors studied had any appreciable effect on the rate of thermal chlorination, some attention was given to the photochemical reaction in the liquid phase. The preliminary results (Table IV and Fig. 3) indicated that light was effective in accelerating the reaction, that the ratio of surface

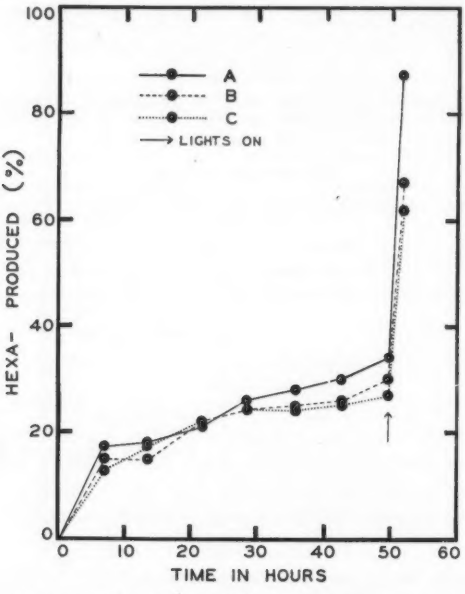

FIG. 3. *Production of hexachloroethane at 100° C. from chlorine-saturated tetrachloroethane in the dark and during exposure to seven 500 w. lamps. (A, B, and C designate different pieces of apparatus; A had a slightly larger surface to volume ratio).*

to volume of the reacting liquid may have effect on the rate, and that 100° C. was the preferable temperature for the reaction. Further work was confined, therefore, to an evaluation of the photochemical production of hexachloroethane from chlorine-saturated liquid tetrachloroethane.

Materials and Analytical Methods

Initially a fraction of crude tetrachloroethane boiling at 144° to 148° C. was used. However, as a result of anomalous rates (Fig. 4,*A*) with this material, the pure material boiling at 146.3° C. was used for further work. The pentachloroethane used was similar to that described in the thermal studies.

The rate of production of hexachloroethane was again determined by measurements of the boiling point of the reacting mixture in an apparatus of the type previously described.

TABLE IV

EFFECT OF LIGHT AND TEMPERATURE ON THE RATE OF FORMATION OF HEXACHLOROETHANE FROM TETRACHLOROETHANE

Lighting condition	Temperature, ° C.	Degrees of freedom	Average rate	Standard deviation
Morning (sunlight)	100	38	3.9	1.9
Afternoon (diffused daylight)	100	26	0.9	0.91
Night (without artificial illumination)	100	11	0.6	0.47
Light-proof chamber	100	17	0.8	0.94
Morning (sunlight)	100	8	2.5	0.63
One 500 w. incandescent lamp	100	4	18.3	5.2
Seven 500 w. incandescent lamps	43	1	19.3	—
Seven 500 w. incandescent lamps	100	4	22.2	4.0
Seven 500 w. incandescent lamps	B.p.*	2	12.7	8.1
Seven 500 w. incandescent lamps	B.p.†	2	4.4	3.3

* *Heating by open flame.*
† *Heating in oil-bath.*

Apparatus

The photochlorination cell was essentially similar to that shown in Fig. 2 except that the reaction chamber consisted of a Pyrex flask 8 cm. in diameter with a flat Corex glass bottom, the top being drawn down for attachment to the condenser and chlorine inlet. All portions of the apparatus except the bottom plate were painted black to prevent the entry of stray light. The reaction chamber was enclosed in an air cabinet regulated to the desired temperature (75° or 100° C.) and the bottom of the chamber was approximately seven inches from the centre of a Mazda incandescent lamp (200 or 500 watts). These lamps emitted rays from 2850Å to beyond 6000Å, were operated slightly below 110 v., without a filter between the lamp and the reaction vessel, and were maintained at a constant intensity by a Corning filter transmitting 3300 to 3900Å, a photocell, a galvanometer, and a variable resistance.

Chlorination Procedure

This was essentially similar to that previously described, the only difference being exposure of the reaction chamber to constant light sources and variations in depth of the reacting mixture.

Results

(1) The Light Absorbed

A spectrograph was used in an attempt to determine the wave-lengths absorbed by the reacting mixture, i.e., the wave-lengths that may have been effective in accelerating the reaction. Tetra- and pentachloroethane, and a 50–50 solution of hexa- in tetrachloroethane were all transparent to light in

the region 3150 to 6000Å, but saturation of these solutions with chlorine rendered them opaque to wave-lengths from 3150 to 4600Å. This roughly corresponds to the absorption range observed for chlorine gas (1). It has been reported that di-, tri-, tetra-, penta- and hexachloroethane are transparent to mercury lines 3650Å and 4360Å, but that the presence of chlorine renders these solutions opaque to these wave bands (2).

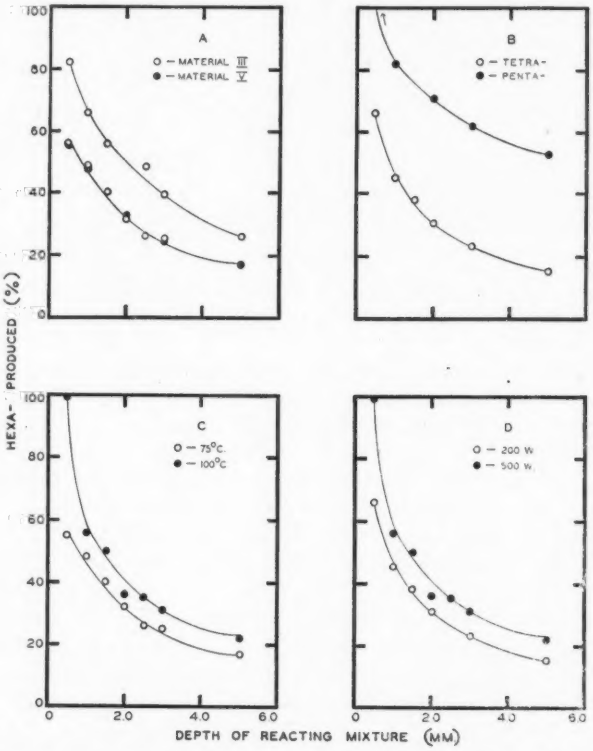

FIG. 4. *The effect of depth of chlorine-saturated tetrachloroethane and other factors on the rate of production of hexachloroethane.*

A. Exceptional rates with less pure material (III) shown in comparison with rates for more highly purified material (V).

B. Production of hexa- from penta- and tetrachloroethane at 100° C. using a 200 w. lamp.

C. Production of hexa- from tetrachloroethane at 75° and 100° C. using a 500 w. lamp.

D. Production of hexa- from tetrachloroethane at 100° C. using a 500 and a 200 w. lamp.

(2) *The Effect of Purity of the Starting Material*

Rate determinations were made using different volumes of tetrachloroethane in the reaction flask. The results are given as the per cent hexachloroethane in the reacting mixture after 30-min. periods for the various depths of the reacting mixture used (with 0.5 ml. layers only a 15 min. reaction

period could be used, but the results have been calculated to a 30 min. basis). The first rate measurements with tetrachloroethane boiling at 144° to 148° C. showed this material to have variable reaction rates (Fig. 4,*A*). Determinations with material of high purity indicated that a slow rate was typical of hexachloroethane production in the absence of impurity.

(*3*) *Comparison of Rates Using Penta- and Tetrachloroethane*

While no pentachloroethane was found when fractionating partially chlorinated samples of tetrachloroethane, it was possible that the chlorination was a two stage reaction, the tetra- first going to penta- and the penta- then forming hexachloroethane at a slower rate. However, chlorinations using these two materials showed that hexachloroethane was formed from penta- about two and one-half times as fast as from tetrachloroethane (Fig. 4, *B*). This indicated that, if a two stage reaction were occurring, the second stage had little significance in determining reaction rates.

(*4*) *Effect of Temperature*

The curves in Fig. 4, *C*, show the effect of temperatures of 75° and 100° C. on the photochlorination. It is evident that an increase in temperature in this range caused an increase in the rate of production of hexachloroethane. Generally about 25% more material was produced at the higher temperature in the same reaction time. When calculating a temperature coefficient for practical use (1.10), differences in the solubility of chlorine in tetrachloroethane at the two temperatures were neglected.* This value is of the same order as the value of 1.16 reported for chlorination, by addition, of tetrachloroethylene (4), of 1.13 for chlorination of dichloroethylene to tetrachloroethane (5, 6), of 1.21 for the chlorination of trichloroethylene to pentachloroethane (6), and 1.12 for the bromination of tetrachloroethylene (10).

(*5*) *Effect of Light Intensity*

The effect of light intensity is shown in Fig. 4, *D*. The reaction rate in the presence of the 500 w. lamp was only 1.3 times that with a 200 w. lamp. The ultra-violet intensity in the region 3300 to 3900Å from the 500 w. lamp was found to be 1.7 times that from the 200 w. lamp. Since the square root of this intensity ratio was the same (1.3) as the rate ratios, it was believed that the reaction rate varied as the square root of the incident light intensity. A similar observation had been made previously for the chlorination of tetrachloroethylene (4).

(*6*) *Effect of Depth of Reacting Mixture*

The curves shown in Fig. 4 clearly depict the pronounced decrease in reaction rate that resulted from increase in depth of the reacting mixture. From the results shown, calculations have been made to indicate the produc-

** A solubility value at 100° C., of 0.16 moles of chlorine per litre of tetrachloroethane had been determined. This was verified by data kindly supplied by the Electrochemical Department of the E. I. du Pont de Nemours and Co., Inc. From the data supplied, a solubility, at 75° C., of 0.27 moles per litre was calculated by interpolation.*

tion occurring in each ½-mm. layer, assuming that no mixing occurred between layers of the liquid. The results of these calculations (Fig. 5) show that, regardless of the temperature and light intensity used, the rate of conversion became negligible when the depth of liquid exceeded 1 mm. The decrease in rate between the first and second ½-mm. layers indicated that only 20% of the most effective light passed the first ½ mm. of the reacting mixture. The

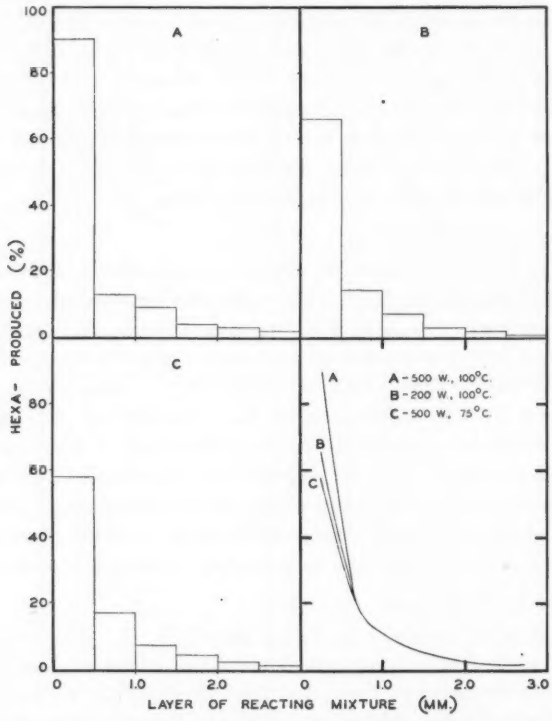

FIG. 5. *Production of hexa- in respective layers of chlorine-saturated tetrachloroethane (calculated from values shown in Fig. 4) at temperature and lighting conditions noted.*

less pronounced decrease in rate in the succeeding layers may result from a slight activity of the less highly absorbed wave-lengths of the activating light or from agitation of the liquid by the incoming gas. It is of little importance, however, since less than 10% of the product was formed in these layers.

Calculations utilizing a solubility value at 100° C. of 0.16 moles of chlorine per litre of tetrachloroethane, the foregoing evidence, and the extinction data for chlorine gas (1) indicated that rays between 3150Å and 3540Å were most effective in accelerating this substitution reaction. This is somewhat lower than the wave-length used for addition reactions (4, 5, 6, 10).

Acknowledgments

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REDUCTION OF SPATIAL TEMPERATURE VARIATIONS IN AIR-COOLED STORAGE ROOMS. II.[1]

By J. W. Hopkins[2], T. A. Steeves[3], and W. H. Cook[4]

Abstract

Measurements made under a series of imposed conditions of heat load, dunnage spacing, and air flow were in agreement with previous work in this laboratory in demonstrating (*a*) the occurrence of appreciable permanent temperature gradients in material, whether exothermic or not, stacked in an air-cooled storage room, and (*b*) the possibility of markedly reducing these gradients by effective channelling of air through the stack. With end-to-end circulation, blocking of voids in the room was the most important single factor in minimizing intra-stack temperature differentials under the conditions of these tests. Further improvement was effected by the provision of optimum dunnage and by augmenting the air flow. It is to be inferred that with blocked voids, dunnage should be extended to all external surfaces of the stack. The desirability of uniform transverse and vertical distribution of the circulating air was also evident. Further trials on a larger scale are required to explore the practical implications of these findings.

Introduction

A previous communication from these laboratories (4) described measurements of spatial temperature variations in an experimental storage room provided with bottom-to-top air circulation. Tests were made first in the empty room, then after introducing a false load of empty boxes to obstruct the air flow, and finally after the addition of known stack heat loads generated by electrical elements placed centrally in the first layer of boxes. Presence of the boxes, even without heat, was found to increase significantly the spatial variation in temperature. Addition of heat, as expected, accentuated this effect. It was found that blocking all voids surrounding the stack itself led to a significant reduction in the spatial temperature differences within the stack. Even more pronounced reductions (of the order of 60%) resulted from the provision of dunnage spacing between each horizontal layer and also between each pair of vertical piles of boxes.

It is now desired to report upon a further and more extensive series of observations made in a somewhat larger experimental storage room. In these trials the preceding bottom-to-top air flow was replaced by an end-to-end circulation more characteristic of large warehouses, and the experiments comprised various stack heat loads, dunnage spacings, and air flows. The results demonstrate that, under the conditions specified, blocking of the voids above and at the side was by far the most important single factor in reducing

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Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa. Issued as Paper No. 163 of the Canadian Committee on Food Preservation, and as N.R.C. No. 1435.

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[4] *Director.*

the accumulation of heat within the stack. Further reductions resulted from dunnage spacing (which was optimum in the vicinity of $\frac{3}{8}$ to $\frac{1}{2}$ in.) and from increased air flow. It is also shown that a major part of the spatial temperature differences recorded within the stack took the form of systematic gradients, transverse and vertical as well as longitudinal, and some of the features of these characteristic of various operating conditions are investigated analytically by a series of plane sections of isothermal surfaces.

Experimental

The experimental room, which was of about 1600 cu. ft. capacity, measured internally 16 ft. in length, 13 ft. in width, and 8 ft. in height. It was insulated by a 4 in. layer of cork. Wooden boxes of size 1 by 1 by 2 ft. were stacked in the room 12 long, 5 wide, and 6 high, giving a stack of dimensions 12 by 10 by 6 ft. exclusive of dunnage. Dunnage (spacing strips) was applied in both the horizontal and vertical plane to each vertical group of six boxes individually, and was also applied externally to the top, bottom, and sides of the stack. A free space of rather more than 3 ft. at the front end of the stack accommodated an exhaust blower refrigerator coil centrally located and discharging through a sheet metal duct past one side of the stack into a smaller free space, rather less than 1 ft. across, between the back of the stack and the rear wall of the room. One side of the stack was positioned $1\frac{1}{2}$ in. plus dunnage from the side wall of the room. Insulating board placed 1 in. plus dunnage from the opposite side of the stack created a void roughly 3 ft. across between this and the opposite wall. Through this void, which was obstructed by baffles at the front and rear (but not at the top) of the stack in order to prevent "short circuiting" of the air circulation, passed the above-mentioned air duct. The combined effect of these features was to leave free spaces of approximately 3 ft. at the front, 2 ft. at the top, 1 ft. at the back, and $1\frac{1}{2}$ to 1 in. plus dunnage at the two sides of the stack. A spacing similar to the last, namely, 1 in. plus dunnage, was also maintained between the bottom of the stack and the floor. All boxes in the stack were equipped with electrical heating elements connected in five parallel series along the length of the stack and so installed as to ensure the generation of equal amounts of heat in all boxes at all dunnage spacings. Thermocouples were installed at each of 23 positions in the stack as specified in Table I, and also in the exhaust and discharge air ducts. The complete experimental arrangement is shown schematically in Fig. 1.

Two series of observations were made. For the first the system was operated at stack heat loads of 0, 432, and 864 B.t.u. per hr. in conjunction with air flows of 500, 710, and 920 c.f.m., dunnage widths of $\frac{1}{8}$, $\frac{3}{8}$, and $\frac{3}{4}$ in., and with the voids above and at the side of the stack both open and blocked. For the second the voids above and beside the stack were blocked throughout but air flows of 290, 500, 710, 920, and 1130 c.f.m. were employed in conjunction with stack heat loads of 0, 432, and 864 B.t.u. per hr. as before, and with dunnage widths of 0, $\frac{1}{4}$, and $\frac{1}{2}$ in. The variable stack heat loads specified were of course additional to the more or less constant amounts entering from

without through the walls and generated inside the room by the fan motor. Calculations based on recorded differences between inlet and exhaust air temperatures indicated that these latter, which may perhaps be termed the

TABLE I

CO-ORDINATES OF LOCATIONS OF THERMOCOUPLES IN STACK, RELATIVE TO POINT SHOWN AS BOTTOM LEFT-HAND CORNER IN FIG. 1 (PLAN)

Thermocouple No.	Co-ordinates, ft.		
	Longitudinal	Transverse	Vertical
1	1.0	1.0	5.0
2	1.0	9.0	5.0
3	1.0	5.0	3.0
4	1.0	1.0	1.0
5	1.0	9.0	1.0
6	3.0	5.0	4.5
7	3.0	2.5	3.0
8	3.0	7.5	3.0
9	3.0	5.0	1.5
10	6.0	1.0	5.0
11	6.0	9.0	5.0
12	6.0	5.0	3.0
13	6.0	1.0	1.0
14	6.0	9.0	1.0
15	9.0	5.0	4.5
16	9.0	2.5	3.0
17	9.0	7.5	3.0
18	9.0	5.0	1.5
19	11.0	1.0	5.0
20	11.0	9.0	5.0
21	11.0	5.0	3.0
22	11.0	1.0	1.0
23	11.0	9.0	1.0

"maintenance heat load," averaged about 1600 B.t.u. per hr. with the voids open and about 1900 B.t.u. per hr. with the voids blocked, the difference of 300 B.t.u. per hr. presumably representing the extra mechanical work required to maintain the same air circulation against increased resistance. The maximum stack heat load was thus of the order of 50% of the maintenance load.

Blocking of the voids was effected as in the earlier experiments (4) by the inflation of suitably sized latex-coated shelter duck bags. Insulating board was interposed to maintain a space of 1 in. plus dunnage between these and the top of the stack. Ideally therefore air should have flowed with equal freedom over the top, bottom, and internal side surfaces. Actually, circulation was to some extent impeded above the stack by heater connections, and below it by thermocouple leads. With the voids blocked, therefore, the four surfaces in question were classified in the following order of increasing impedance to air flow: (i) outer side (adjacent to wall); (ii) inner side (adjacent to insulating board); (iii) top; (iv) bottom.

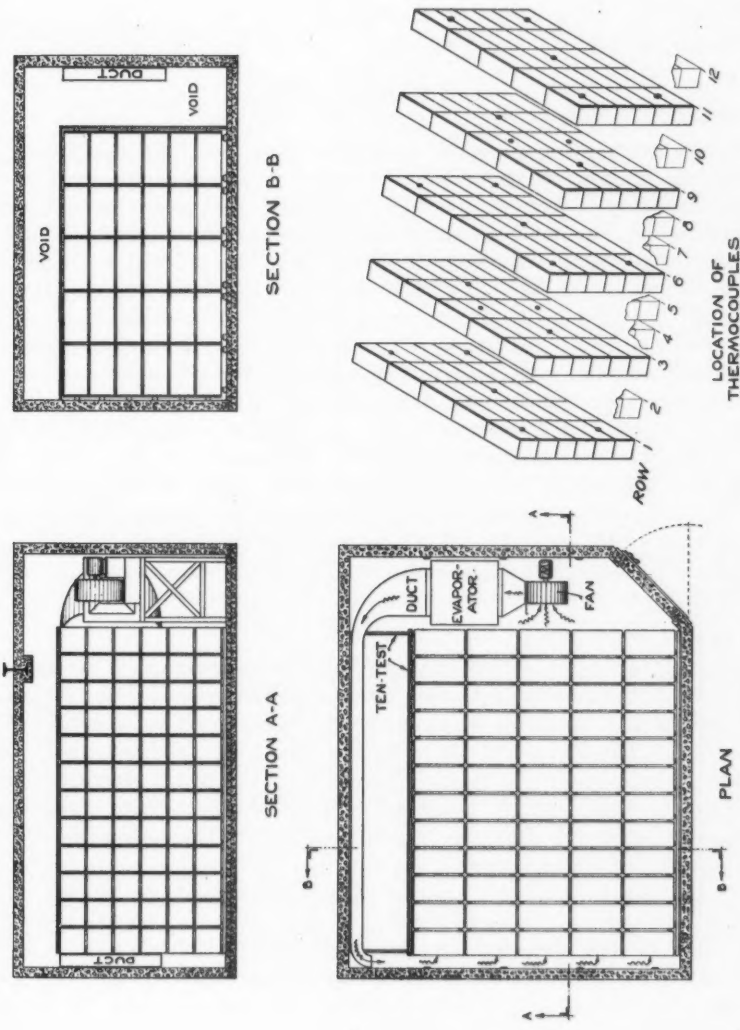

FIG. 1. *Schematic diagram of test room and stack of boxes.*

After the imposition of any selected set of conditions the system was operated for several hours (usually overnight) until equilibrium was attained. Ten readings of each thermocouple were then made at 20-min. intervals and averaged to yield a mean value characteristic of the position in question. Analysis of the entire series of observations thus involved the statistical reduction of some 23,000 individual items.

Results

Assessment of Significance

Although every effort was made to operate under controlled conditions of temperature, air flow, and heat load, for a variety of reasons this aim proved to be impossible of complete achievement, and the precise temperature gradients within the stack characteristic of any particular set of imposed conditions were never completely reproducible. The residual uncontrolled variation although generally small and of random incidence was statistically significant, and in these circumstances it was necessary to have recourse to the theory of errors for assessment of the data. The method adopted was to subject any function of the observations selected for study to an analysis of variance procedure (1, 2, 3) in which second-order interactions and differential effects, including the above-mentioned uncontrolled residual fluctuations, were used to test the statistical significance of differences in the averages of the main factors or their first-order interactions. The findings may conveniently be considered under the three headings of (*a*) total spatial temperature variance within the stack, (*b*) the proportion of this occurring in the form of systematic temperature gradients, and (*c*) the characteristics of such gradients.

Total Spatial Temperature Variation

The standard, i.e., root-mean-square, deviation of the average reading of each of the 23 thermocouples located within the stack was used as a measure of over-all spatial variation in temperature. This provides a satisfactory index of the relative variability encountered under different conditions imposed. It requires to be noted, however, that as a major portion of the variation in question proved to be systematic, the absolute values obtained in this way are applicable only to the particular ordered arrangement of the thermocouples adopted in these tests.

The main trends observable are summarized in Tables II to IV and illustrated in Fig. 2, *A–D*. Table II and Fig. 2, *A–B*, indicate that blocking the upper and side voids, thus forcing more of the circulated air to pass through the stack, markedly reduced the spatial variation at all three stack heat loads, including zero. It is to be noted, however, that whereas with the voids blocked minimum variation was recorded at $\frac{3}{8}$ in. dunnage, with the voids open the widest spacing used ($\frac{3}{4}$ in.) gave the least variation, suggesting that in this circumstance still wider spacing might have been advantageous. Table III and Fig. 2, *C*, obtained by combining relevant portions of both the first and second series of experiments, permit a comparison of six dunnage

TABLE II

INDEX OF SPATIAL TEMPERATURE VARIATION (STANDARD DEVIATION IN DEG. F.) FOR VARIOUS CONDITIONS OF DUNNAGE, AIR FLOW, AND HEAT LOAD

Dunnage, in.	Air flow, c.f.m.	Voids open				Voids blocked			
		Stack heat load				Stack heat load			
		0	432 B.t.u./hr.	864 B.t.u./hr.	Average	0	432 B.t.u./hr.	864 B.t.u./hr.	Average
1/8	500	2.3	2.9	3.7	2.95	0.7	1.5	2.2	1.47
	710	2.4	2.9	3.2	2.80	0.9	1.8	2.5	1.76
	920	2.0	3.1	3.6	2.89	0.4	1.8	2.4	1.52
	Average	2.23	2.93	3.44	2.87	0.67	1.71	2.36	1.59
3/8	500	2.6	3.1	3.8	3.14	0.8	1.2	1.2	1.08
	710	2.8	3.0	3.2	3.01	0.6	0.8	1.1	0.83
	920	2.6	2.6	3.2	2.78	0.5	0.7	0.9	0.71
	Average	2.64	2.90	3.39	2.98	0.64	0.91	1.07	0.87
3/4	500	2.3	2.7	2.8	2.59	1.2	1.5	1.8	1.17
	710	1.9	2.4	2.7	2.33	0.8	1.3	1.5	1.22
	920	2.0	2.3	2.5	2.27	0.9	1.2	1.2	1.11
	Average	2.07	2.45	2.67	2.40	0.98	1.33	1.52	1.28
Average		2.32	2.76	3.18	2.75	0.77	1.32	1.65	1.24

Necessary difference (5% level of statistical significance) between averages of 3 = ± 0.30.
Necessary difference (5% level of statistical significance) between averages of 9 = ± 0.17.
Necessary difference (5% level of statistical significance) between averages of 27 = ± 0.11.

TABLE III

INDEX OF SPATIAL TEMPERATURE VARIATION (STANDARD DEVIATION IN DEG. F.) UNDER SPECIFIED CONDITIONS OF DUNNAGE AND HEAT LOAD.

(AVERAGES FOR AIR FLOWS OF 500, 710, AND 920 C.F.M. VOIDS BLOCKED)

Stack heat load, B.t.u./hr.	Dunnage spacing, in.					
	0	1/8	1/4	3/8	1/2	3/4
0	0.75	0.68	0.74	0.64	0.67	0.98
432	1.90	1.71	1.47	0.91	0.83	1.33
864	3.15	2.36	1.97	1.07	1.02	1.52

Necessary difference for 5% level of statistical significance = ± 0.28.

spacings ranging from 0 to 3/4 in., with the voids blocked. Under these conditions, optimum dunnage was clearly in the neighbourhood of 3/8 to 1/2 in., whilst the effect of reducing this spacing became progressively more pronounced with increasing heat load. Table IV and Fig. 2, *D*, constructed entirely from the second series of trials, show that increasing the air flow

TABLE IV

INDEX OF SPATIAL TEMPERATURE VARIATION (STANDARD DEVIATION IN DEG. F.) UNDER SPECIFIED CONDITIONS OF AIR FLOW AND HEAT LOAD.

(AVERAGES FOR 0, ¼, AND ½ IN. DUNNAGE. VOIDS BLOCKED)

Air flow, c.f.m.	Stack heat load, B.t.u./hr.		
	0	432	864
290	1.25	2.12	2.94
500	0.92	1.58	2.41
710	0.65	1.32	1.90
920	0.60	1.31	1.84
1130	0.46	1.19	1.70

Necessary difference for 5% level of statistical significance = ± 0.23.

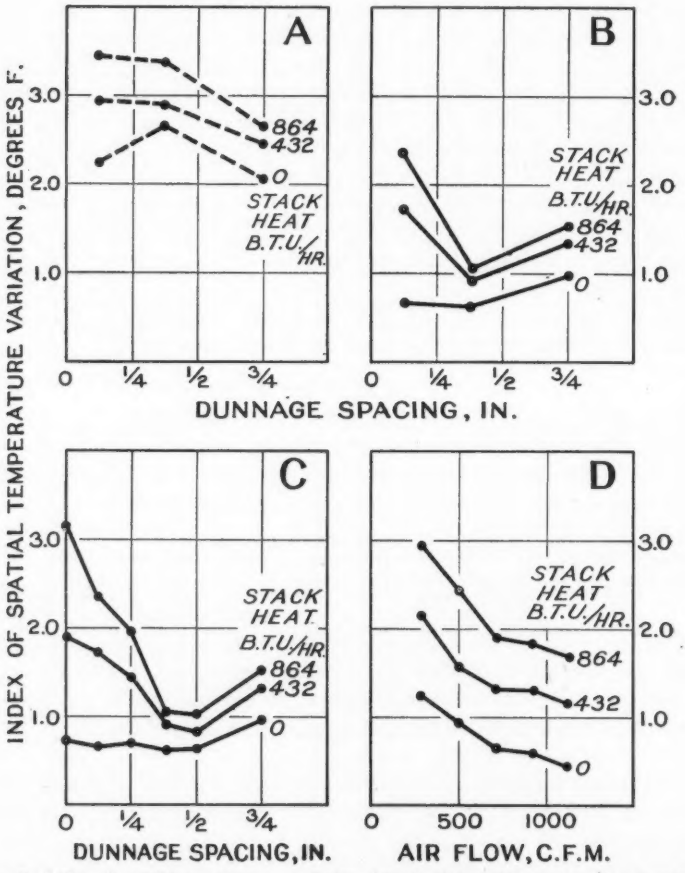

FIG. 2. *Index of spatial temperature variation (standard deviation in deg. F.) in relation to dunnage, heat load, and air flow. A: voids open. B–D: voids blocked.*

from 290 to 1130 c.f.m., i.e., from about 11 to about 40 changes per hour in the empty room, led to a progressive, although not directly proportional reduction in temperature variations. This was true of all the three heat loads and dunnage spacings included in this series.

Temperature Gradients

Systematic elements in the foregoing temperature differences within the stack were investigated by equating the mean temperature t characteristic of each of the 23 measured positions to a general quadratic function of the rectangular co-ordinates x, y, z of the point in question. This equation was of the form:

$$t = a + bx + cy + dz + exy + fxz + gyz + hx^2 + iy^2 + jz^2 + \epsilon \quad (1)$$

Values of the 10 coefficients a–j were determined by the method of Least Squares so as to minimize in turn the sum of the squares of the residuals $S(\epsilon^2)$ for each of the sets of operating conditions included in the experiments. The difference between $S(\epsilon^2)$ and $S(t-\bar{t})^2$, where $\bar{t}$ denotes the average of the 23 recorded mean temperatures, then provided a measure of the proportion of the total intra-stack temperature variance representable by continuous quadratic gradients. This is set forth in the form of percentages in Tables V to VII.

TABLE V

PERCENTAGE OF INTRA-STACK TEMPERATURE VARIANCE REPRESENTABLE BY QUADRATIC GRADIENTS. (AVERAGES FOR $\frac{1}{8}$, $\frac{3}{8}$, AND $\frac{3}{4}$ IN. DUNNAGE AND AIR FLOWS OF 500, 710, AND 920 C.F.M.)

Stack heat load, B.t.u./hr.	Voids	
	Open	Blocked
0*	88	90
432	88	92
864	86	91
Average	87	91

Augmented air flow (Table VI) or heat load in conjunction with $\frac{1}{4}$ in. or less dunnage (Table VII) resulted in some increase in the complexity of the heat distribution, which was accordingly less adequately represented by a quadric surface. In general nevertheless the quadratic function specified in Equation (1) accounted for some 90% of the total intra-stack variance, indicating that by far the greater part of the recorded temperature differences were associated with relatively simple continuous gradients, however different the form of these might be under the various conditions of heat load, dunnage, and air flow. It may be remarked that the terms in xy, xz, and yz in Equation (1) are to be interpreted physically as representing interactions of the linear temperature gradients in the x, y, and z directions. Such interactions would

TABLE VI

PERCENTAGE OF INTRA-STACK TEMPERATURE VARIANCE REPRESENTABLE BY QUADRATIC GRADIENTS.

(AVERAGES FOR 0, $\frac{1}{4}$, AND $\frac{1}{2}$ IN. DUNNAGE. VOIDS BLOCKED)

Air flow, c.f.m.	Stack heat load, B.t.u./hr.		
	0	432	864
290	94	90	93
500	93	90	89
710	91	90	88
920	91	89	90
1130	81	89	87

TABLE VII

PERCENTAGE OF INTRA-STACK TEMPERATURE VARIANCE REPRESENTABLE BY QUADRATIC GRADIENTS.

(AVERAGES FOR AIR FLOWS OF 500, 710, AND 920 C.F.M. VOIDS BLOCKED)

Stack heat load, B.t.u./hr.	Dunnage spacing, in.					
	0	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{3}{8}$	$\frac{1}{2}$	$\frac{3}{4}$
0	92	92	96	87	86	90
432	89	88	91	93	91	94
864	89	86	85	94	93	94

operate to produce for example a modification of the longitudinal gradient as between the bottom and top or one side and the other of the stack. The occurrence of several such interactions was revealed by the analyses of variance. Their numerical magnitude was however in all instances definitely secondary to that of the average linear and quadratic trends.

Characteristics of Temperature Gradients

Tables VIII to X summarize the mean linear gradients deduced from the temperature differences recorded within the stack under various conditions. The mean longitudinal gradients listed range from + 0.64° F. per ft. for a stack heat load of 864 B.t.u. per hr. with the voids open (Table VIII) to + 0.07° F. per ft. for zero stack heat and 1130 c.f.m. air flow with the voids blocked (Table IX). In general the longitudinal gradient was reduced by more than 50% by blocking the voids or by increasing the air flow from 290 to 1130 c.f.m. It was rather less sensitive to variations in dunnage (Table X) but was at a minimum in the region of $\frac{3}{8}$ to $\frac{1}{2}$ in. The mean linear transverse and vertical gradients were for the most part small in magnitude and fluctuated irregularly in sign, indicating that the temperature differences recorded in these directions were distributed fairly symmetrically about the centre of the

TABLE VIII

MEAN LINEAR TEMPERATURE GRADIENTS (DEG. F. PER FT.). AVERAGES FOR $\frac{1}{4}$, $\frac{3}{8}$, AND $\frac{3}{4}$ IN. DUNNAGE AND AIR FLOWS OF 500, 710, AND 920 C.F.M.

Stack heat load, B.t.u./hr.	Longitudinal		Transverse		Vertical	
	Voids		Voids		Voids	
	Open	Blocked	Open	Blocked	Open	Blocked
0	+0.47	+0.13	+0.16	−0.03	−0.38	+0.01
432	+0.58	+0.24	+0.19	−0.06	−0.37	+0.04
864	+0.64	+0.34	+0.21	−0.10	+0.20	+0.06
Average	+0.56	+0.24	+0.19	−0.06	−0.13	+0.04

Necessary difference for 5% level of statistical significance: Longitudinal, ±0.04; transverse, ±0.02; vertical, ±0.04.

TABLE IX

MEAN LINEAR TEMPERATURE GRADIENTS (DEG. F. PER FT.). AVERAGES FOR 0, $\frac{1}{4}$ AND, $\frac{1}{2}$ IN. DUNNAGE. VOIDS BLOCKED

Air flow, c.f.m.	Longitudinal			Transverse			Vertical		
	Stack heat load, B.t.u./hr.			Stack heat load, B.t.u./hr.			Stack heat load, B.t.u./hr.		
	0	432	864	0	432	864	0	432	864
290	+0.27	+0.41	+0.54	−0.02	+0.02	+0.03	−0.11	−0.09	+0.27
500	+0.16	+0.29	+0.41	−0.02	−0.06	−0.05	−0.12	−0.03	+0.05
710	+0.18	+0.27	+0.34	+0.01	−0.04	−0.07	−0.07	+0.01	+0.01
920	+0.11	+0.22	+0.29	+0.00	+0.01	+0.02	+0.01	+0.02	+0.04
1130	+0.07	+0.21	+0.24	+0.00	+0.02	+0.07	+0.01	−0.01	−0.00

Necessary difference for 5% level of statistical significance; longitudinal, ± 0.07; transverse, ± 0.05; vertical, ± 0.14.

TABLE X

MEAN LINEAR TEMPERATURE GRADIENTS (DEG. F. PER FT.) AVERAGES FOR AIR FLOWS OF 500, 710, AND 920 C.F.M. VOIDS BLOCKED

Dunnage, in.	Longitudinal			Transverse			Vertical		
	Stack heat load, B.t.u./hr.			Stack heat load, B.t.u./hr.			Stack heat load, B.t.u./hr.		
	0	432	864	0	432	864	0	432	864
0	+0.15	+0.29	+0.42	−0.10	−0.12	−0.14	−0.08	−0.08	−0.02
$\frac{1}{8}$	+0.09	+0.25	+0.44	−0.10	−0.23	−0.36	+0.09	+0.10	+0.11
$\frac{1}{4}$	+0.20	+0.32	+0.40	+0.05	−0.04	−0.04	−0.07	−0.05	−0.08
$\frac{3}{8}$	+0.12	+0.21	+0.26	−0.01	−0.00	−0.01	+0.16	+0.06	+0.05
$\frac{1}{2}$	+0.10	+0.17	+0.23	+0.05	+0.07	+0.08	+0.06	+0.08	+0.17
$\frac{3}{4}$	+0.19	+0.26	+0.33	+0.03	+0.06	+0.08	−0.13	−0.08	−0.04

Necessary difference for 5% level of statistical significance: Longitudinal, ± 0.06; transverse, ± 0.06; vertical, ± 0.10.

stack. They, however, present no information respecting the pronounced curvature actually characteristic of these gradients. This was examined analytically as described below.

If t is given some constant value such as $t_0 + 1$, where t_0 is the mean temperature of the cold air entering the room from the delivery duct, and if ϵ is neglected, then Equation (1) specifies the quadric surface approximating most closely to the actual surface generated by the aggregate of points within the stack at the temperature $t_0 + 1$. This may be termed the isothermal surface of $+ 1°$. Similarly equating t to $t_0 + 2$, $t_0 + 3$, $----t_0 + n$ leads to the isothermal surfaces of $+ 2°$, $+ 3°$, $----+ n°$. Figs. 3 to 7 illustrate some of the characteristics of these surfaces under different experimental conditions by longitudinal, transverse, and vertical plane sections through the central axes of the stack.

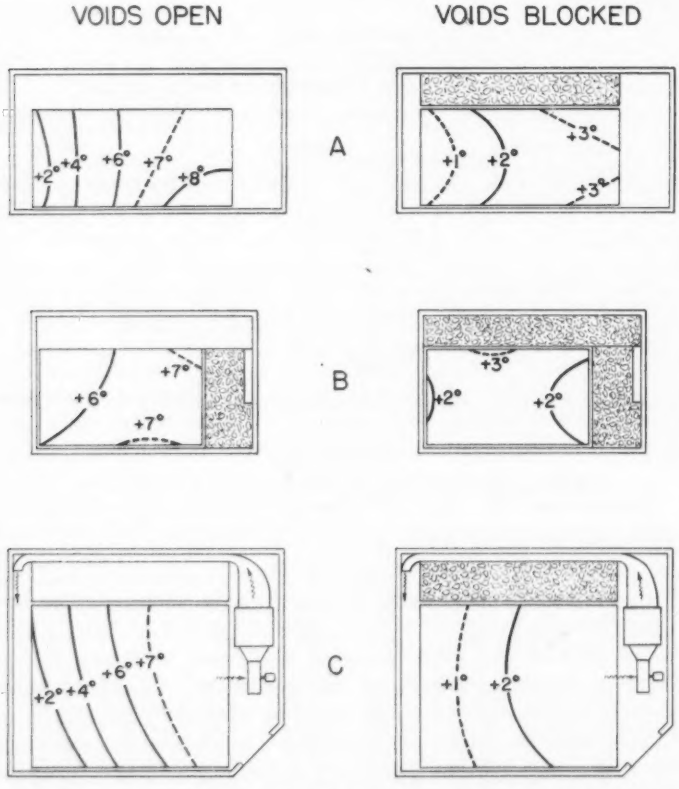

FIG. 3. *Plane sections of isothermal surfaces. A: central longitudinal vertical section. B: central transverse vertical section. C: central longitudinal horizontal section. Averages for air flows of 500, 710, 920 c.f.m., heat loads of 0, 432, and 864 B.t.u. per hr., and* $\frac{1}{8}$, $\frac{3}{8}$, *and* $\frac{5}{8}$ *in. dunnage.*

A considerable number of the surfaces obtained were sectors of hyperboloids of one sheet. They thus exhibited anticlastic ("saddle-shaped") curvature, presumably owing to the fact that cold air circulated across the sides of the stack more freely than across the top or bottom. However, the general breaking down of temperature gradients by an air flow of 1130 c.f.m. with the voids blocked resulted in an "open" isothermal surface for + 2° F. which was approximated by the portion of a hyperboloid of two sheets illustrated in Fig. 6. Various segments of ellipsoids also resulted.

Fig. 3 portrays the marked decrease in both magnitude and complexity of temperature gradients resulting from blocking the voids and thereby channelling circulating air more effectively through the stack. Also to be noted is the asymmetry of the temperature gradients obtained with the void open. It would appear that in this circumstance, the non-central location of the discharge duct tended towards an orientation of the air circulation across and over the surface of the stack. This characteristic was largely, although not completely, eliminated by blocking the voids, the previously noted differential impedance of air movement across the top, bottom, and sides of the stack still remaining operative. The foregoing effects are observable in more detail in Figs. 4 and 5. These also illustrate the building up of temperature

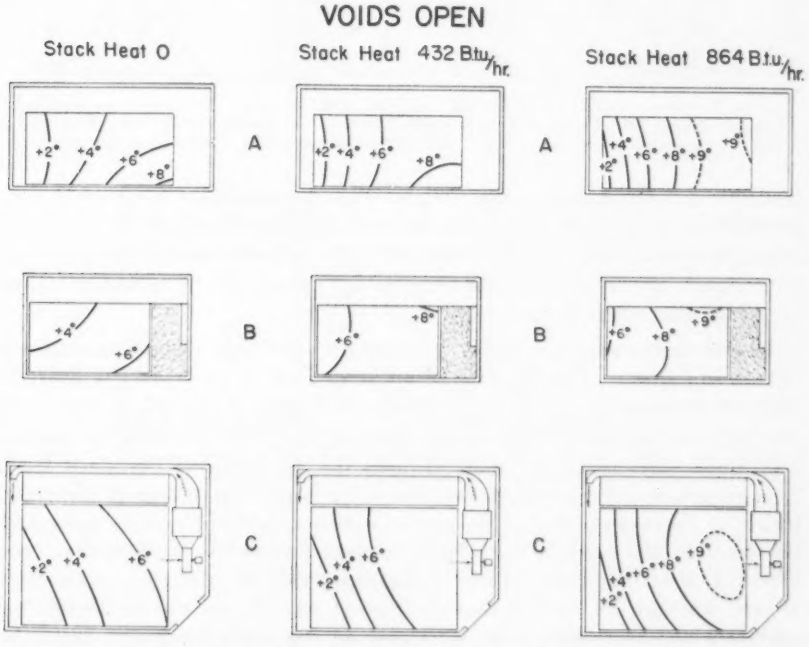

FIG. 4. *Plane sections of isothermal surfaces, voids open. A: central longitudinal vertical section. B: central transverse vertical section. C: central longitudinal horizontal section. Averages for air flows of 500, 710, and 920 c.f.m. and* $\frac{1}{8}$, $\frac{3}{8}$, *and* $\frac{3}{4}$ *in. dunnage.*

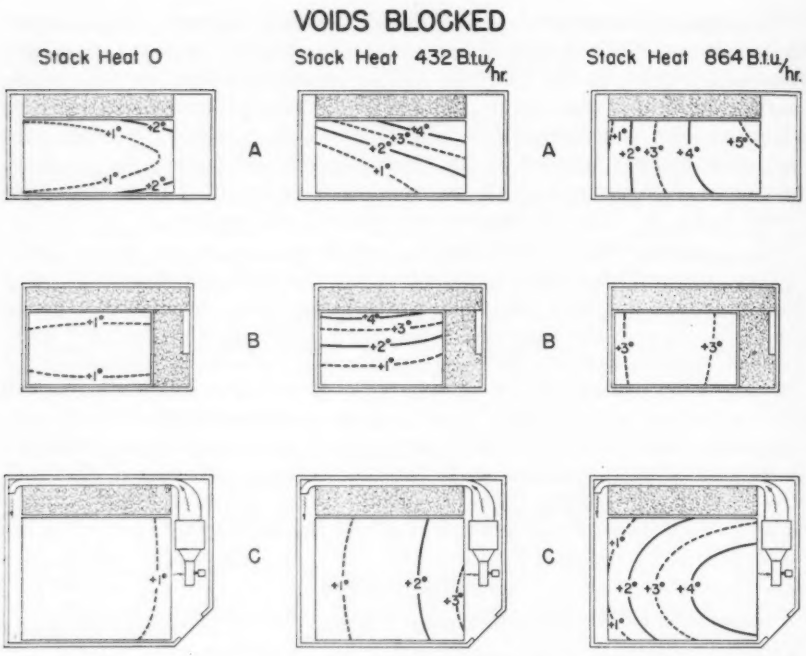

FIG. 5. *Plane sections of isothermal surfaces, voids blocked. A: central longitudinal vertical section. B: central transverse vertical section. C: central longitudinal horizontal section. Averages for air flows of 500, 710, and 920 c.f.m. and $\frac{1}{8}$, $\frac{3}{8}$, and $\frac{3}{4}$ in. dunnage.*

gradients by stack heat loads, whilst Fig. 6 exemplifies their reduction, particularly in the central zone of the stack, by augmented air flow. Fig. 7 shows the average gradients recorded with the voids blocked for zero, $\frac{3}{8}$ and $\frac{3}{4}$ in. dunnage, the second of these being in the vicinity of the optimum for the operating conditions of these tests.

This optimum was presumably occasioned by the balancing of two opposed factors as follows. Maintenance of an extra inch or $1\frac{1}{2}$ in. of free space in addition to dunnage at the top, bottom, and sides of the stack must have resulted in a correspondingly greater part of the total circulated air passing over these surfaces rather than through the apertures in the stack itself. This in turn would lead to relatively more accumulation of heat in the centre which, in the event of the stack apertures being small, would more than offset the effect on the external surfaces of radiation from the walls, ceiling, and floor. The left-hand side of Fig. 7 illustrates this effect in the extreme case of zero dunnage, i.e., no internal aperture at all. As the size of the internal apertures was increased, more air traversed the stack internally, and $\frac{3}{8}$ in. dunnage sufficed to reduce temperatures at the centre below those at the periphery, as shown in the middle portion of Fig. 7. On the other hand,

increasing the width of the apertures by additional dunnage must have correspondingly reduced the linear velocity associated with the circulation of a specified number of cubic feet of air per minute, until eventually a point was reached at which this became a limiting factor, and a further accumulation of

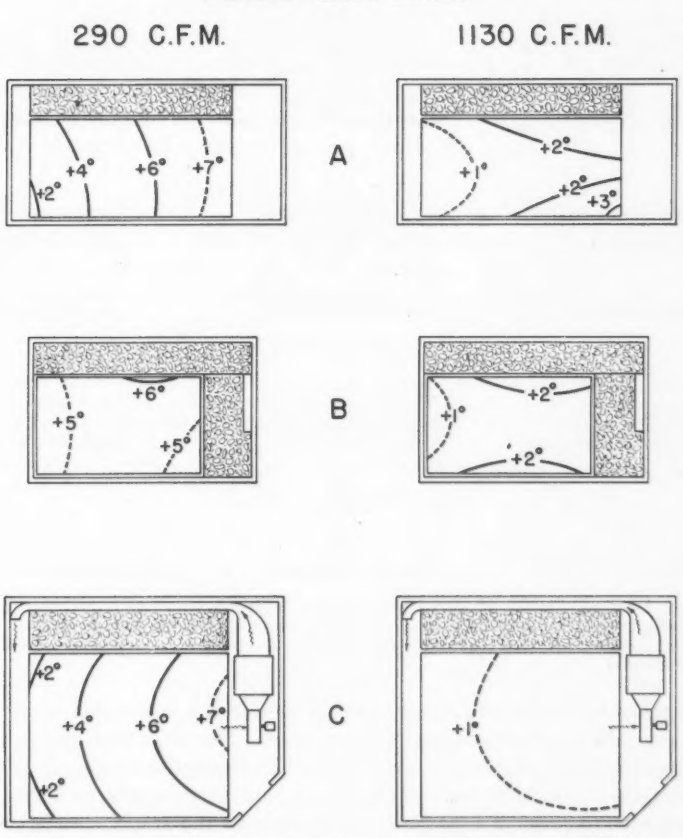

FIG. 6. *Plane sections of isothermal surfaces, voids blocked. A: central longitudinal vertical section. B: central transverse vertical section. C: central longitudinal horizontal section. Averages for heat loads of 0, 432, and 864 B.t.u. per hr.*

heat, particularly peripherally but to some extent internally as well, became manifest. This would appear to be the situation exhibited in the right hand portion of Fig. 7.

It will be appreciated that the quadric surfaces delineated in Figs. 3 to 7 are only second-degree approximations to the actual isothermal surfaces generated within the stack. From Tables V to VII, however, it is clear that

they must in fact portray fairly closely most of the recorded temperature gradients. In general these gradients were characterized by more pronounced curvature in the vertical than in either the horizontal or transverse planes,

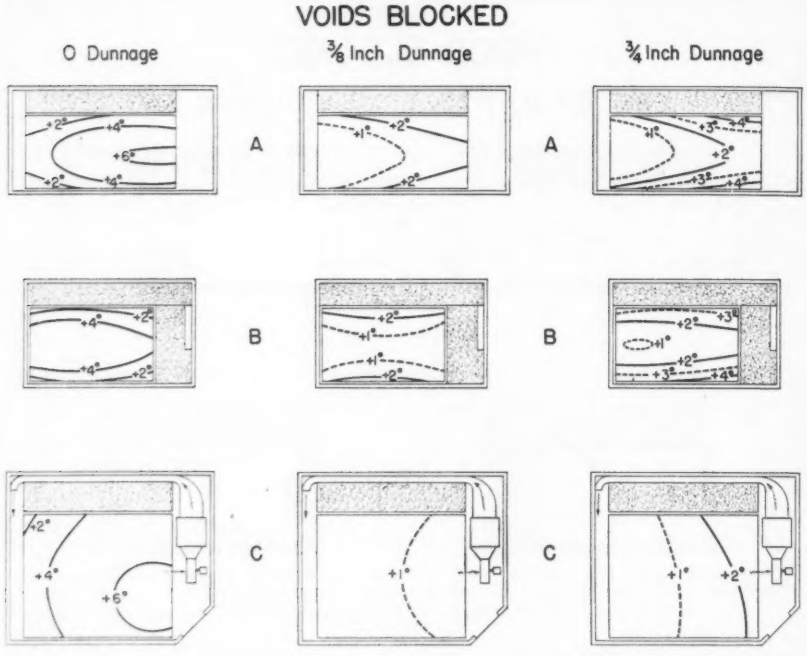

FIG. 7. *Plane sections of isothermal surfaces, voids blocked. A: central longitudinal vertical section. B: central transverse vertical section: C: central longitudinal horizontal section. Averages for heat loads of 0, 432, and 864 B.t.u. per hr. and air flows of 500, 710, and 920 c.f.m.*

presumably as a further consequence of the unequal restriction of air movement over the top, bottom, and side surfaces. Dunnage eliminating vertical and transverse gradients and reducing all isothermal surfaces to planes at right angles to the direction of air flow would be desirable as indicative of uniform effectiveness of heat removal throughout the stack. An approximation to this might perhaps be achieved by using different widths of dunnage at the centre, periphery, and exterior, although the requirements would almost certainly be modified by any alteration in the size or shape of the stack or in the location of inlet and exhaust ports.

Conclusions

It is concluded that these experiments were in agreement with previous work in this laboratory in demonstrating (*a*) the occurrence of appreciable permanent temperature gradients in material, whether exothermic or not,

stacked in an air-cooled storage room, and (*b*) the possibility of markedly reducing these gradients by effective channelling of air through the stack. With end-to-end circulation, blocking of voids in the room was the most important single factor in minimizing intra-stack temperature differentials under the conditions of these tests. Further improvement was effected by the provision of optimum dunnage and by augmenting the air flow. It is to be inferred that with blocked voids, dunnage should be extended to all external surfaces of the stack. The desirability of uniform transverse and vertical distribution of the circulating air was also evident. Further trials on a larger scale are required to investigate the extent to which the present results were a function of the size and shape of the stack, and also to determine the most suitable ratio of external to internal dunnage.

Acknowledgments

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A CLINOMETER FOR MEASURING SMALL ANGLES[1]

By R. H. Field[2]

Abstract

The paper describes a clinometer for the accurate measurement of angles of elevation or depression up to 5° from the horizontal. The geometrical design permits a theoretical precision of ± 2″ to be attained in this range on a uniformly divided micrometer head without the application of corrections or the use of cams or associated devices. While the instrument can be read to 1″ and is sensitive to about twice this amount, no special tools or jigs were needed for its construction, beyond the equipment ordinarily available in a small machine shop.

Purpose

During the adjustment and calibration of certain types of fire-control equipment, it is necessary to measure small angles of elevation or depression (usually less than 5°) to a precision of two or three seconds of arc. In the Canadian services it has been customary to rely principally on the old Watkin type clinometer for all angle measurements in a vertical plane; but this instrument is subject to the acquisition of serious periodic errors, and it was probably never expected to work to the precision under consideration. The new clinometer, described below, filled the need, and has been found quite suitable, for example, in calibrating or forming correction elements provided in fire-control apparatus to compensate for the curvature of the earth. For this work, hitherto, somewhat elaborate collimator or other equipment had been necessary.

Principle

The micrometer screw is the usual element employed in a self-contained clinometer for the measurement of small angles. Kinematically, the design of this class of clinometer can be considered by reference to a simple triangle, *A B C*, Fig. 1. The side *a* represents the contact plane which rests on the

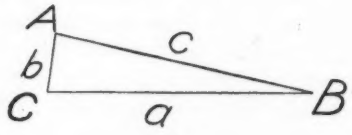

Fig. 1.

surface of which the inclination to the horizontal is to be measured. A level vial is attached to the side *c* which is brought to the horizontal by means of a micrometer screw represented by the side *b*. *B* is the measured angle.

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The designer has the choice of various possibilities. If C be made and fixed as a right angle, c remain of constant length and the nut be fixed to c, a uniformly graduated micrometer head on b will actually indicate, to some scale, the quantity sin B. Consequently, if the scale be adjusted to read angles correctly at 0° and 5°, the theoretical error in the indications (nominally subdivided equally in angle) will be at any measured angle θ:

Error = 18,000 cosec 5° (sin θ − 0.2 θ° sin 5°) seconds of arc.

This error is shown graphically in Curve A, Fig. 2. The Watkin clinometer has a vertical, fixed, micrometer screw, but the side c, Fig. 1, is variable in length, and the graduations on the micrometer drum are not uniform, so that the simple theory does not apply.

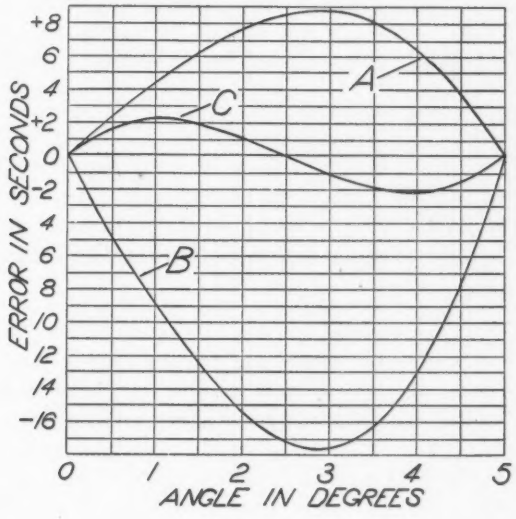

FIG. 2.

As an alternative, A may be fixed at 90° and b hinged at C while c still remains constant in length. In this case the indications will be proportional to tan B. A clinometer of this form, adjusted at 0° and 5° as before, would indicate angles with an error:

Error = 18,000 cotan 5° (tan θ − 0.2 θ° tan 5°) seconds.

This error is shown graphically in Curve B, Fig. 2.

Both curves, A and B, show errors undesirably large for the purpose in view, and a modification of the second scheme was considered in which the angle A was made 87.5°, b was hinged at C, and the end of c moved along a at B. The simple analysis showed that this design, for a range of 5°, should make possible a maximum error of ± 2″ (i.e., corresponding to two-thirds

of an inch in one mile) in the readings of a uniformly graduated micrometer drum, compared with respective maxima of + 9″ and − 17″ for the two cases previously considered. Actually, the theoretical error in the third case, with the same provisions as before would be:

$$\text{Error} = 18{,}000 \operatorname{cosec} 5° \cos 2\overset{\circ}{.}5 \{ \sin\theta \sec (2\overset{\circ}{.}5 - \theta) - 0.2\,\theta° \sin 5° \sec 2\overset{\circ}{.}5 \} \text{ seconds.}$$

Description

In order to gain advantage of the attainable precision indicated by the small theoretical error, care was taken during the mechanical design to reduce the possibility of secondary errors arising from the functioning of the parts. A complete clinometer, as finally designed by the author and built in the Instrument and Model Shop of the National Research Laboratories, Ottawa, is shown in Fig. 3. Fig. 4 is a "close up" of the micrometer screw end of the instrument, while Figs. 5 and 6 are drawings to illustrate details.

Base

The base is a bronze casting, shaped at the bottom to give a bearing surface (scraped flat) of 2 by $6\frac{3}{4}$ in., to conform to Army requirements. The centre portion is cored to save weight and the ends are machined for the fittings described below. Guards are screwed to the micrometer end and the two sides of the base to protect the measuring parts against damage.

Inclinable Platform

This is also a bronze casting, bearing two posts for carrying the level vial housing, one end of which is tapped for two opposing screws, bearing against the post for windage adjustment. The vial has a value of 10 sec. per division. At the hinge end of the platform a longitudinal groove is machined to locate the hinge piece, and the other end is bored and split to receive the nut.

Micrometer

Referring to Fig. 5, *A* is the steel micrometer screw, which is 0.56 in. diam. and has 40 t.p.i. It works in the split nut, *B*, 1.1 in. long. Screw *A* is bored and reamed up the centre and at the end of the reamed hole a hard steel piece, *C*, is inserted, having its lower face flat and polished. This face rests on the steel bearing ball, *D*, peened into the centre of the top of the pivot, *E*, which is a good fit in the axial hole in the screw. To free *E* from constraint as to inclination, its lower end is made spherical in shape, and rests in the cup, *F*. A pin, *G* engaging in a slot in the spring-loaded cover, *H*, prevents axial rotation of *E*. The micrometer drum is held in place by friction when the finger knob, *I*, is tightened by the central screw tapped into the top end of *A*. This permits the zero of the clinometer to be adjusted at any time by slackening the central screw and turning the drum; which is to be preferred over adjustment involving a change in the level vial with respect to the inclinable platform, owing to the inevitable bubble creep that takes place after straining the

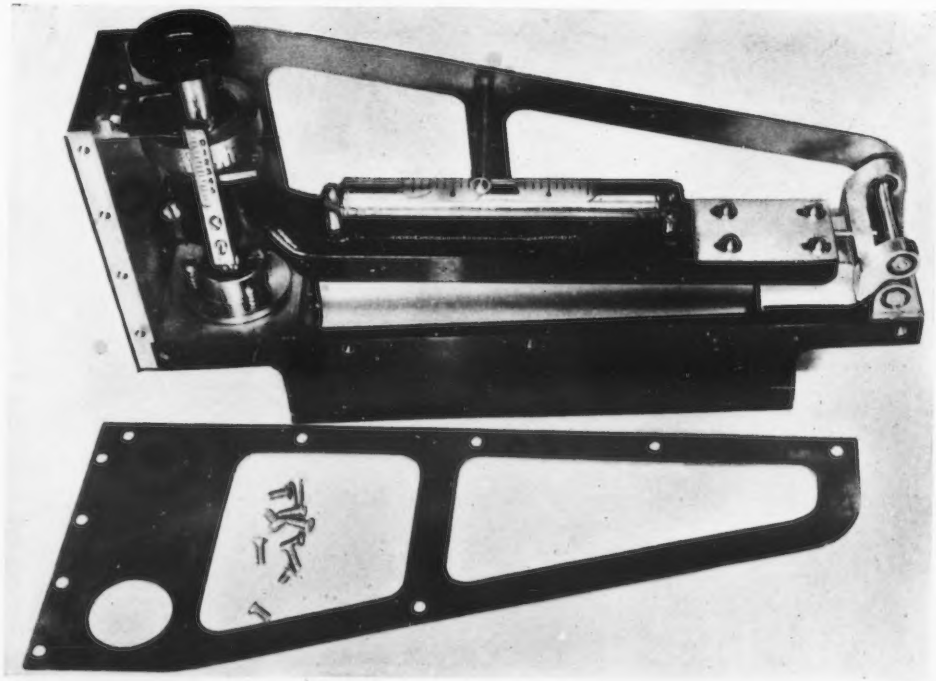

FIG. 3

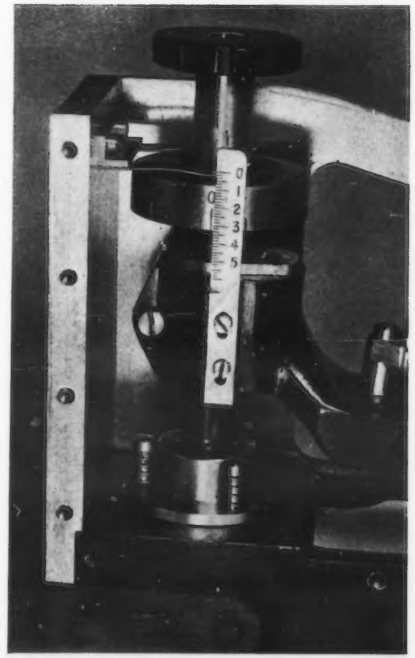

FIG. 4

FIG. 3. *Sensitive clinometer; one side of the guard is removed to reveal details.*

FIG. 4. *Micrometer screw end of sensitive clinometer. In this instance one division on the drum corresponds to 0.2', but later instruments have been made to read directly to 0.1'.*

level-mounting screws. To prevent the micrometer screw from lifting off the pivot, two leaf springs, *J*, bear on a fibre washer on the top of the micrometer drum. The length of the effective lever arm of the clinometer is made and adjusted so that one turn of the micrometer screw corresponds to an angle of 10 min. The drum is divided into 10 major 1′ divisions, and each minor subdivision represents 0′.2. In later instruments the subdivisions have been made 0′.1 in value, and by estimation readings are easily made to 0′.02 (or 1″).

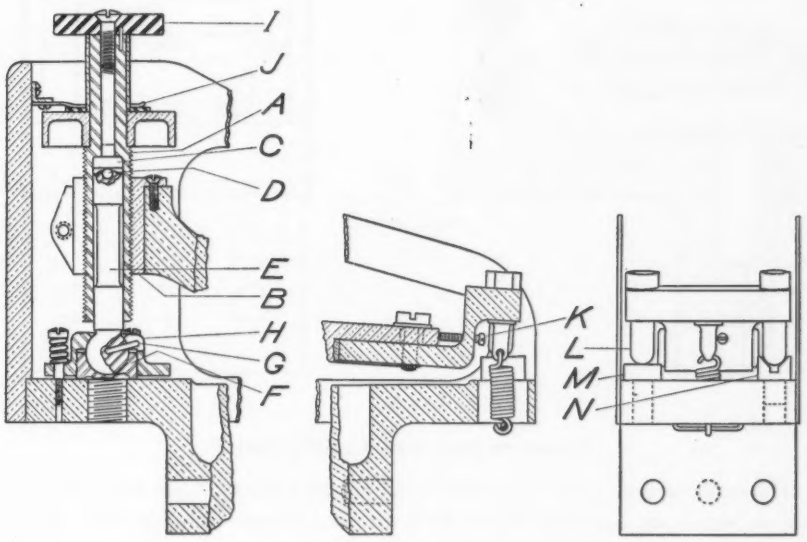

FIG. 5.

Hinge

To facilitate the adjustment of the effective lever arm, the hinge piece is attached to the inclinable platform by screws passing through slotted holes in the platform. A screw, *K*, tapped in the hinge piece, with the end contacting the platform, was found very convenient in adjusting the clinometer in the laboratory.

In the first model the hinge piece was fitted with two steel pins, *L*, having hardened hemispherical ends; one pin resting on the hard flat insert, *M*, and the other on the grooved insert, *N*. Closure was maintained by a coil spring. In a later model, an alternative device, Fig. 6, is used. The hinge piece and the base are both fitted with housings for 0.375 in. O.D. ball bearings. A link, *O*, has four round portions turned on it, each to fit the bore of the bearings and so as to yield two horizontal axes spaced 0.8 in. apart. This later form of hinge is cheaper, and as the bearings can be packed with, say, vaseline,

it is thought there is less possibility of troubles due to corrosion. Experience alone will show whether there is any advantage of one form of hinge over the other.

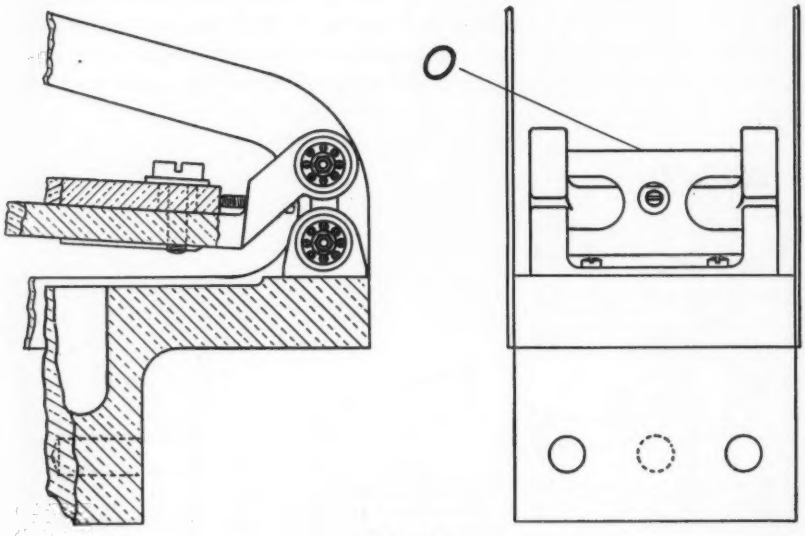

FIG. 6.

Construction and Calibration

The construction in the shop presented no difficulties. Care was taken to cut the screws on a good lathe and both screws and nuts were lapped to spare units before running them together.

For the adjustment and calibration use was made of an angle-head reading to seconds, and described in a separate paper (1). First the effective length of the inclinable platform was adjusted by trial to give the minimum corrections over the range 0 to 5°. Then a check was made at each 30′ interval in this range, together with a test at each 0.2′ throughout one complete turn of the micrometer screw at 0°, 2.5°, and 4°. From repeating the tests, it would appear that these clinometers can be adjusted to yield uncorrected readings accurate to 5″, while with the application of corrections and the exercise of care as to alignment and other precautions inherently necessary in any method of measuring angles to the precision of a few seconds, angles can be measured to a precision of 2 or 3″. The calibration corrections for one of these clinometers, determined when new, are given below. This particular instrument was damaged in Army service, and after repair and recalibration the corrections were found to agree to ± 2″ with the original ones, determined some four years earlier.

SENSITIVE CLINOMETER No. 2

Calibration corrections

Error in seconds of arc at given readings

Scale reading	Micrometer drum reading									
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0° 00′	0		+2		+2		+1		+2	
0 30	0									
1 00	+2									
1 30	+2									
2 00	+1									
2 30	0	+2		+3		+3		+1		
3 00	−2									
3 30	−2									
4 00	−2		−2		−3		−5		−4	
4 30	−1									
5 00	0									

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TWO ACCESSORIES FOR THE ELECTRON MICROSCOPE LABORATORY—(A) SPECIMEN STAGE (B) PLATE READER[1]

By W. M. Barss[2]

Abstract

A new electron diffraction specimen stage is described which may be used in place of the standard RCA diffraction stage to permit five independent transmission type diffraction patterns to be obtained without opening the vacuum system. The modification of a commercial microfilm reader for use in measuring electron diffraction patterns is also reported.

I. A Multiple Diffraction Specimen Stage for the Electron Microscope

In a series of experiments involving the identification of powdered materials by electron diffraction pictures of the transmission type it was found desirable to load several specimen holders at once and to provide means for interchanging them inside the vacuum system. Fig. 1 illustrates the design of a multiple specimen stage constructed to replace the diffraction specimen stage supplied with the RCA Type EMU-1 electron microscope, and Fig. 2 shows its external appearance.

Parts corresponding to RCA stock parts for the regular stage were used whenever possible: this applies particularly to the design of the external and internal vacuum seals. The slide *a* carries five of the standard transmission apertures and specimen holders and moves horizontally in a slot in the supporting piece *b*, which is held in the correct position in the stage body *c* by means of a set screw and the aligning key *d*. The slide is moved by the pin *e* in the end of the push rod *f* and is positioned by a spring-loaded detent *g* engaging notches in the edge of the slide. The handle *h* aids in inserting the stage into the microscope. The parts are of brass with the exception of the rubber vacuum gaskets and the steel push rod, key, ball bearing, and two compression coil springs. External surfaces are nickel plated.

The device has been found to operate well. It does not affect the evacuation time of the microscope appreciably, and the lubricated rubber packing provides a satisfactory vacuum seal for the well polished push rod. The holes and notches in the slide are located with sufficient accuracy that it is unnecessary to adjust the electron beam position when specimens are changed. Since a standard specimen such as gold leaf may be kept in one of the five specimen holders and its diffraction pattern obtained under conditions identical with those for the other specimens, it is convenient to register on each plate a standard pattern to be used for calibration.

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Contribution from the Division of Physics and Electrical Engineering, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1433.

[2] *Physicist.*

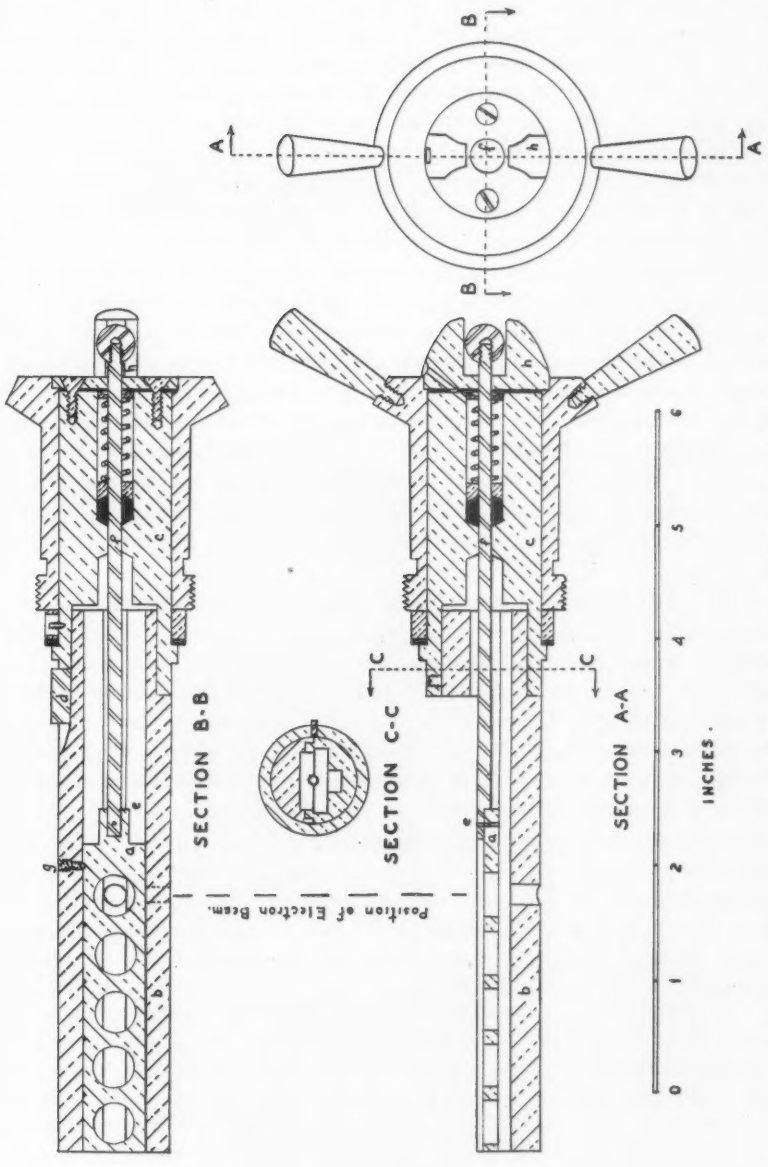


FIG. 1. *Multiple diffraction specimen stage, sectional drawing.*

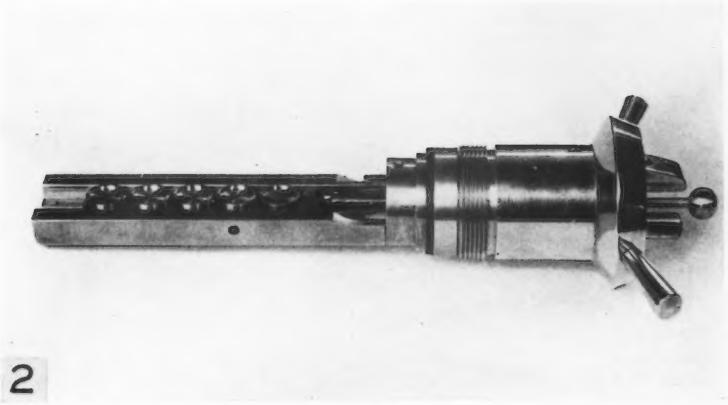
II. Projector for Electron Diffraction Patterns

The electron diffraction patterns obtained with the RCA Type EMU-1 electron microscope are so small that it is difficult to measure ring diameters with as great accuracy as desirable without using a magnifier of some kind. The type of comparator commonly used for measuring spectroscopic plates has too high a magnification for this service, as the field of view is too small and the visibility of weak rings is greatly reduced. It has been found that slight modification of a commercial microfilm reader gives an instrument that projects a magnified image of the diffraction pattern upon a translucent screen, where measurements may be readily made with a ruler.

The microfilm reader used for this purpose was made by the Society for Visual Education, Chicago, a portable type, RM, which uses two mirrors to throw the projected image upon the ground glass screen forming the front of the case. The film reels and film advance mechanism were replaced by an adjustable frame into which the 2 by 10 in. plates used in the electron microscope may be inserted. The original lens (approx. 50 mm. focal length) was replaced by an 80 mm. lens (a 3 in. projector lens is equally suitable) giving a magnification of about $7\frac{1}{2}$ times. The aperture of the lens system is not sufficiently large to cover the whole area exposed in the microscope but does cover a circle of diameter approximately 4 cm., which is adequate for most work.

In order to minimize distortion in the projected image, the effective axis of the projection lens, as reflected by the mirrors, should fall normally upon the viewing screen. It was found that the axis could be made to lie in a vertical plane through the centre of the screen, but not readily in the normal plane having a horizontal intersection with the screen at its centre. Because of the resulting distortion in the vertical direction all patterns to be measured are made concentric about a mark at the centre of the screen, and measurements are made along the horizontal diameters of the rings.

When a diffraction adapter was introduced for the first RCA electron microscopes it was pointed out that the smallness of the angles involved permitted reduction of the diffraction equation to the simple form $D\,d = 2\,k\,\lambda\,L$ (2), where D is the diameter of the diffraction ring corresponding to the lattice spacing d, L is the distance between the specimen and the photographic plate, λ is the de Broglie wave-length of the electrons, dependent upon the accelerating voltage, and k is an instrumental constant dependent upon the diffraction lens power. It is convenient to combine the factors on the right-hand side of the above equation into a single quantity K which will remain constant as long as specimens are placed in the same position, the high voltage does not vary, and the lens setting is unchanged. It has become the practice in this laboratory to expose a standard diffraction specimen, usually gold, with each group of other specimens in order to check the calibration and find the amount of variation to be expected in the value of K.



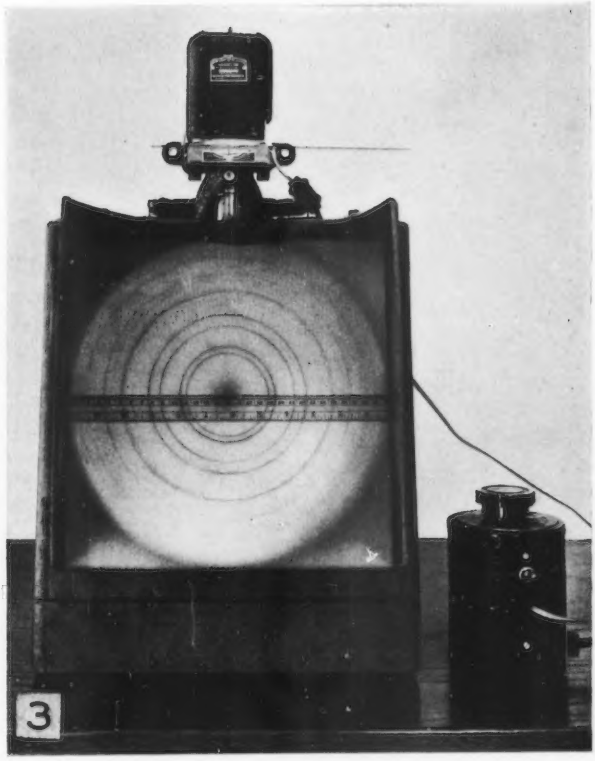


FIG. 2. *Multiple diffraction specimen stage.*
FIG. 3. *Projector for electron diffraction patterns.*

The value of the product $D \times d$ has been found to change slightly for larger values of D because of the inaccuracy of the approximation for larger diffraction angles, and possibly because of distortion introduced by the lens used in measuring the plates. A diffraction pattern of gold was therefore measured over as wide a range of ring diameter as possible. Results are given in Table I. The lattice spacings were calculated from the lattice constant $a = 4.0702$ Å (1).

TABLE I

MEASUREMENT OF GOLD DIFFRACTION PATTERN (PROJECTED)

Reflection indices, hkl	Lattice spacing d in Å (10^{-8} cm.)	Ring diameter, D, cm.	Product $D \times d$ in 10^{-8} cm.^{2}
111	2.350	7.75	18.21
200	2.035	8.95	18.21
220	1.438	12.65	18.19
311	1.226	14.85	18.21
222	1.174	15.50	18.20
400	1.017	17.90	18.20
331	0.934	19.50	18.21
420	0.910	20.00	18.20
422	0.831	21.9	18.20
333/511	0.784	23.2	18.19
440	0.719		
531	0.688	26.3	18.1
442/600	0.678		
620	0.643	28.2	18.13

* Average value for first 10 rings, $K = 18.202 \pm 0.003$

The values of $D \times d$ are seen to be quite consistent up to projected ring diameters of about 25 cm., and the deviation is only about 0.5% for the largest rings. Experience has shown that lattice spacings of unknown materials may be calculated, using such a calibration, with an error of about 0.5% or better.

Acknowledgments

The author wishes to acknowledge the assistance of Mr. H. A. MacDonald in the design and construction of the multiple diffraction specimen stage.

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RECENT DESIGN OF A SMALL TELEPHONE MAGNETO[1]

By D. S. Smith[2]

Abstract

An example is given of the product obtained by applying modern methods in permanent magnet design to the problem of constructing a hand driven magneto of about flashlight battery size. The method of arranging the mechanical parts to conform with the electromagnetic system is described.

During the past few years, there have been tremendous improvements in permanent magnet materials. These have been closely followed by improved design methods. Thus it is now usually possible to predetermine closely the characteristics of a device using a permanent magnet in its magnetic circuit, and to design the device for minimum magnet size by direct, as opposed to cut-and-try methods (1).

An interesting problem in the design of such a device for use in a rather special application was presented to the author in the form of a request for a telephone magneto to meet very limited space requirements. The dimensions and output called for were as follows:

Outside diameter	1 7/16 in.
Length	$2\frac{5}{8}$ in. approximately
Output	10 v. minimum with a load of 500 ohms.

It will be noted that this is very little larger than an ordinary flashlight battery. The small diameter presented a problem and first rough designs on paper were most unattractive. However, it soon became apparent that the use of two annular magnets with the armature in between would result in a workable design, and, once the general physical arrangement was settled upon, a detailed design soon followed.

Fig. 1 shows details of the pilot model, which differed only in minor details from the initial design. The two magnets are Alnico II and are of manufacturer's stock size. The remainder of the magnetic circuit (the two pole pieces and the rotor) is of ordinary mild steel. The two bearings are of the Oilite type and are pressed into the magnets. To simplify winding of the armature two stub shafts are used instead of a through shaft. These stub shafts are spigotted to the armature and held with screws.

The rotor is driven manually through an epicyclic gear train with a drive ratio of 5.8/1. Some difficulty was encountered at first when using a single planetary gear. This was satisfactorily overcome by using three planetary gears, thus eliminating any tendency for the gears to bind.

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Contribution from the Division of Physics and Electrical Engineering, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1423.

[2] *Formerly Electrical Engineer, National Research Laboratories, Ottawa; now with the Northern Electric Company, Vancouver, B.C.*

The two pole pieces are pulled tight over the magnets by means of the four brass screws, which also serve to hold the complete assembly together. The magneto was designed to fit into a non-magnetic case with a screw-on end-cover. The handle and planetary gear assembly are mounted directly on the end-cover, as shown in Fig. 1.

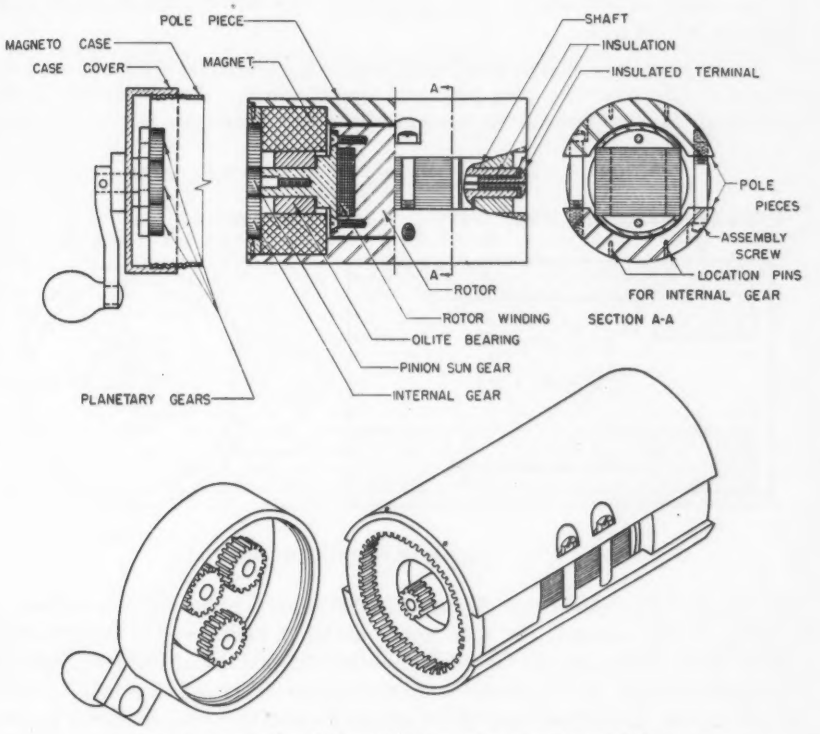

FIG. 1. *Sectional and isometric views of the complete assembly.*

The design of the magnetic circuit was determined to a very marked extent by the over-all dimensions and further by the dimensions of available magnets. It was desirable that the magnets as finally used have almost the same dimensions as a type available commercially, since any excess material must be removed by grinding. Apart from these considerations the peculiar configuration of the magnetic circuit made design to usual criteria difficult. In spite of this the output was predetermined with a reasonable degree of accuracy, after somewhat arbitrary allowances were made for leakage.

The permanent magnet alloy, Alnico II, was chosen because its high energy content and good remanence characteristic permitted a small volume of the material to deliver the required working flux. In addition, it was desirable that the material used have resistance to the demagnetization caused by stray

fields, vibration, shock, and temperature changes. The high coercive force characteristic of Alnico II makes it particularly suitable for such an application.

Data on probable load resistances indicated that these might range from 500 to 10,000 ohms, and it was decided to design for maximum power output in the region of 500 ohms. This resulted in the use of approximately 3500 turns of No. 38 wire.

Magnetizing was undertaken in a specially built magnetizer with poles fitting closely over the pole pieces of the magneto. The positions of the poles and the flux paths after removal of the magnetizer are shown in Fig. 2.

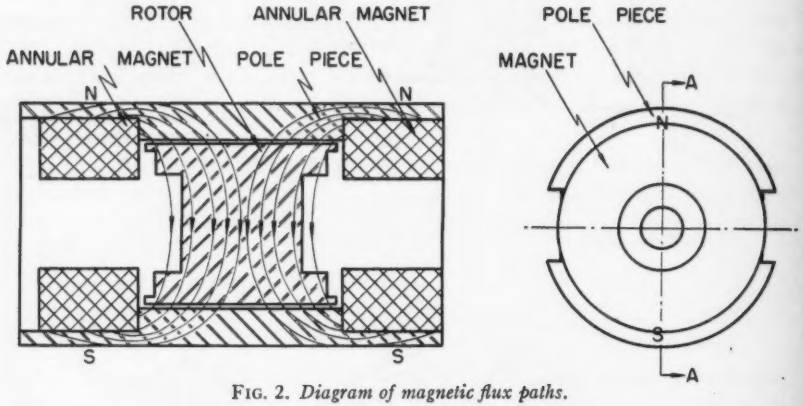

FIG. 2. *Diagram of magnetic flux paths.*

The design called for a flux density of 6000 lines per sq. cm. at the neutral section of the magnet. It was not considered necessary to stabilize the magnets after magnetizing, since a higher than normal initial voltage presented no disadvantage. In the initial state of magnetization and at a handle speed of 100 r.p.m. the output was 30 v. on open circuit. After allowing for the reduction in output that occurs as the magnets become stabilized, the capacity of the magneto is still easily capable of meeting the operating requirements.

An interesting sidelight was the subsequent discovery of a very similar piece of German equipment that was apparently used as a generator with a tachometric gun-sight. The general configuration of the magnetic circuit was identical, differences being largely in minor details. For instance, a non-magnetic band, crimped in place was used to hold the assembly together. This method was first considered for the design described here, but later discarded in favour of the assembly screw method shown above.

Reference

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